VOL. XVI. NOVEMBER, 1894. NO. 11.

THE JOURNAL

OF THE

AMERICAN CHEMICAL SOCIETY.

[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF PURDUE UNIVERSITY.]

A METHOD FOR DETERMINING CALCIUM OXIDE IN QUICKLIME.

BY W. E. STONE AND F. C. SCHEUCH.

Received September 1, 1894.

THE value of quicklime is based upon the amount of calcium oxide which it contains. This value may be diminished by the presence of other substances originally present in the limestone, consisting usually of magnesia, alumina, silica, and iron; by incomplete ignition in the lime-kiln, on account of which some calcium carbonate fails to be converted into calcium oxide; and lastly, by a partial "slaking," by which a portion of the calcium oxide reverts to calcium carbonate.

An analysis of quicklime, therefore, should show not only the amount of calcium present in distinction from other elements, but should distinguish between the calcium as oxide and other forms of combination. The customary gravimetric method, based upon solution of the calcium compounds in acids, precipitation as calcium oxalate, ignition, etc., attains only the first of these requirements and affords no data for judging of the original condition of the calcium thus found. Consequently this method may furnish erroneous conclusions with regard to the commercial value of the material examined.

The method here proposed enables one to determine with a high degree of accuracy and rapidity the actual amount of calcium oxide in quicklime. It is based upon the well-known fact that

the alkaline earths form definite compounds with sucrose, called saccharates. Several such compounds are known with barium and strontium. With calcium oxide, sucrose forms at least three compounds, the mono-, di- and tricalcium saccharates, containing respectively one, two, and three molecules of calcium oxide to one of sucrose. The two first are formed when quicklime is dissolved in the cold in a sucrose solution. On heating this to boiling, a precipitate is thrown down consisting in the main of the tricalcium saccharate.

Numerous authorities may be quoted with regard to the solubility of calcium oxide in sucrose solutions of which the two following will suffice for citation.

Berthelot[1] gives the maximum solubility in solutions of sucrose of varying strength.

Grams sugar in 100 cc...	0.096	0.400	1.058	1.386	2.000	4.850
CaO dissolved.....	0.154	0.194	0.281	0.326	0.433	1.031

The following data are from Schatten.[2]

In ten grams of sugar solution of different percentages:

Per cent.....	1.	4.	8.	12.	16.
Grams CaO dissolved,	0.029	0.080	0.160	0.271	0.394

Numerous other references indicate the ready solubility of calcium oxide in sucrose solutions, and the apparent possibility of applying this fact to the separation of the actual calcium oxide from the other constituents of quicklime, led us to make the following studies:

1. The conditions under which calcium oxide is dissolved in sucrose solutions:

Lamy[3] has shown that solubility varies inversely with the temperature. Ten liters of ten per cent. sucrose solution, at the given temperatures, dissolved the stated amounts of calcium oxide.

Temperature C°.....	0°	15°	30°	50°	70°	100°
Grams CaO dissolved.....	250	215	120	53	23	15.5

For our experiments, pure calcium oxide was prepared by igniting pure calcium carbonate to a constant weight. It was

[1] *Ann. Chim. phys.*, [3], **46**, 176.
[2] Von Lippmann, Die Zucker-Arten, 109.
[3] *La Sucrerie indigene et Coloniale*, **11**, 19.

found by repeated experiment that one gram of this material was easily soluble in 150 cc. of a ten per cent. sucrose solution after agitating fifteen to twenty minutes at ordinary temperature. To accomplish perfect solution it was necessary that the material be finely pulverized. If heat were employed, the lime was converted into a pasty, insoluble mass which, however, dissolved on cooling.

2. The degree of solubility of calcium oxide in sucrose solution. Repeated experiments gave the following results:

One gram of pure CaO was only partly dissolved in 100 cc. of a five per cent. sugar solution.

One gram of pure CaO was only partly dissolved in 150 cc. of a five per cent. sugar solution.

One gram of pure CaO was only partly dissolved in 100 cc. of a ten per cent. sugar solution.

One gram of pure CaO was completely dissolved in 150 cc. of a ten per cent. sugar solution.

From these results it appears that not less than 150 cc. of a ten per cent. solution of sucrose could be safely employed to dissolve the calcium oxide in one gram of quicklime.

3. Behavior of other constituents of quicklime toward sucrose solutions:

Besides calcium oxide, quicklime usually contains more or less iron, alumina, magnesia, and silica. In addition to these, calcium carbonate may also be present. The behavior of these toward sucrose solutions was studied in detail with the following results:

Magnesia. Pure magnesium oxide, specially prepared, was treated with a ten per cent. solution of sucrose. One hundred and fifty cc. of the latter, after shaking with one gram of magnesium oxide for thirty minutes, were filtered and treated with ammonia and sodium phosphate, but only the faintest turbidity resulted. Again, one gram of magnesium oxide was shaken with 150 cc. of sucrose solution, filtered, and the filtrate titrated with standardized hydrochloric acid, and an equivalent of 0.001 gram of magnesia was found, or one-tenth of one per cent. These results show that magnesia is not appreciably soluble under the given conditions. Indeed, the existence of a com-

pound between magnesia and sucrose is doubted. On the other hand, magnesia is said to be freely soluble in a solution of calcium oxide in sucrose.[1] To test this point, mixtures of pure magnesium and calcium oxides were treated with sugar solutions as follows: One-half gram of each were mixed and shaken with 150 cc. of sugar solution. A considerable portion of the material was insoluble. We filtered and titrated the filtrate with standardized acid, the result being an exact equivalent of the calcium oxide employed. Again, one-half gram of each were mixed and treated with sugar solution as before. We filtered and precipitated the calcium from the filtrate by means of ammonium oxalate. The filtrate from this showed only slight turbidity when treated with ammonium and sodium phosphate. These results show that magnesium oxide is not soluble to an appreciable degree in sucrose solution containing calcium oxide, under the stated conditions.

Alumina was found quite insoluble, no appreciable amount being found in the filtered sucrose solution.

Calcium carbonate was also insoluble to any appreciable degree in the ten per cent. sucrose solution under the stated conditions.

Ferric oxide shaken with ten per cent. sugar solution was also insoluble. Schachtrup and Spunt[2] mention that ferric oxide inverts sucrose but not in an alkaline solution. We have verified this by heating a small quantity of ferric oxide with a sugar solution; the latter soon acquired the power of reducing Fehling's solution. But when the same experiment was repeated with the addition of some calcium oxide no inversion occurred. It is evident, therefore, that the iron contained in quicklime would not be affected by sucrose solution.

4. The determination of calcium oxide when dissolved in sucrose solution:

Calcium oxide when dissolved under the preceding conditions admits of determination, either gravimetrically by precipitation as calcium oxalate or volumetrically by titration with hydrochloric acid. Several comparisons of the two methods were made, using known amounts of pure calcium oxide and while

[1] Von Lippmann, *Die Zucker-Arten*, 148.

[2] *Pharm. Cent. Halle*, **34**, 148.

each were accurate to the extent of yielding the theoretical numbers, the volumetric method was found preferable on account of its greater rapidity. For the latter method, standardized hydrochloric acid of about fifth-normal strength was employed, using tropaeolin or rosolic acid as an indicator.

5. Application of the preceding data to the analysis of quicklime.

Following the conclusions derived from the preceding tests, several samples of quicklime were analyzed for calcium oxide. They were all in a fresh state and contained little calcium carbonate.

In each case, approximately one gram of the finely pulverized material was shaken with 150 cc. of a ten per cent. sucrose solution during twenty minutes, the solution filtered and the clear filtrate titrated with standardized hydrochloric acid. At the same time other portions of the same samples were dissolved in hydrochloric acid and the calcium determined in the usual way by precipitation as calcium oxalate. Following are the results:

Sample.	Weight of quicklime taken, grams.	Volume of ten per cent. solution of sucrose taken, cc.	Per cent. CaO by titration method.	Per cent. CaO by gravimetric method.	Variation of volumetric method.
No. 1	1.020	150	92.12	93.00	—0.88
" 2	1.090	150	91.90	92.28	—0.38
" 3	1.006	150	92.15	93.10	—0.95
" 4	1.108	150	95.01	95.90	—0.89
" 5	1.023	150	87.30	87.70	—0.40
" 6	1.232	150	91.70	92.30	—0.60

The results by the sucrose method were in each case slightly lower than by the gravimetric method discrepancy which may be ascribed to a small amount of calcium carbonate present in the sample.

In quicklime which had become partially slaked, this discrepancy would be still greater since the sucrose method would indicate only the actual calcium oxide. Aside from this, the greater ease and rapidity of the latter recommends it in cases where the total calcium is present in the form of the oxide. An entire determination may thus be made in a half-hour with a degree of accuracy quite sufficient for all ordinary purposes.

[Contributions from the Chemical Laboratory of Purdue University.]

A COMPARISON OF METHODS FOR THE DETERMINATION OF STARCH.

By W. E. Stone.

Received September 1, 1894.

THERE is no longer much doubt among chemists that, in food analysis, the present practice of classifying a large number of widely varying substances under the head of non-nitrogenous extract matter, as an homogeneous material, is wholly erroneous and misleading. The variety of substances covered by this term is well known, and, while it is granted that they are mainly of carbohydrate nature, it is equally clear that, so far as food valuation is concerned, there should be some degree of differentiation between sugars, starches, gums, and the more or less soluble forms of cellulose.

The position of the pentosans in this class of bodies has been pointed out in its different aspects by myself and others at intervals during the past four or five years. It has been shown that these bodies form a distinct constituent of the non-nitrogenous extract matter to a greater or less degree in all fodder articles; that under present analytical methods their individuality as food constituents is wholly merged into that of the more valued carbohydrates; some light has also been thrown upon their digestibility, and analytical methods of a fair degree of accuracy have been devised for their estimation in the presence of other similar bodies.

Mention is made of this instance here to show that really some progress has been made, and that too within a short time, in our knowledge of what, until recently, has been an obscure constituent of the non-nitrogenous extract matter.

The object of this present paper is to call attention along the same line to certain proposed methods for the quantitative estimation of probably the most important of these bodies; *viz.*, starch. At first thought it may appear that the existing methods for the determination of starch are sufficiently satisfactory and accurate; and this is, doubtless, true so far as starch alone is

concerned. But it must be remembered that starch almost always occurs in connection with other soluble non-nitrogenous matters, under which conditions its estimation becomes quite another matter and constitutes exactly the question under discussion. The pentosans or gums are, doubtless, the most common of these accompanying substances and, unfortunately for the analyst, behave toward many analytical methods precisely like starch. Hence, a result which is interpreted to mean starch by a strict adherence to the method, may be due, to a very large degree, to other substances. For example, brewers' grains, which from the very process through which they have passed contain little or no starch, will by the ordinary method of inversion and titration be credited with a large amount of starch. Again, hay or straw yield considerable amounts of reducing sugars on inversion, although they contain a minimum of starch, or even none at all. In both these cases the results are due to the inversion of insoluble gums which are present in large quantities.

With these facts in mind it is apparent that a food analysis should give some information with regard to the relative amounts of these different substances present, and should include determinations of the pentosans, sugars, and starches separately.

In this connection the inquiry arises as to how accurately it is possible to determine these bodies as they occur in connection with each other in the ordinary feeding stuffs, by current and accepted methods. As regards the pentosans and sugars, the state of our knowledge seems far more satisfactory than in the case of the starches, in proof of which proposition the following data are offered.

Five methods of starch determination have been compared upon a variety of materials. Four of the methods involve the inversion of the starch and the estimation of the sugar thus formed by volumetric or optical methods; the fourth method is based upon a combination of the starch with one of the alkaline earths. Following are the details of the different methods:

1. Inversion of the starch with hydrochloric acid and titration with Fehling's solution, known as Sachsse's method: Three to five grams of the starch bearing material are heated in a water-bath with 200 cc. of water and twenty cc. of concentrated acid,

during three hours; the acid is neutralized with soda, the solution filled to 500 cc., and titrated with Fehling's solution in the usual manner.

2. Inversion with nitric acid and polarization, proposed by Guichard, *Bull. Soc. Chim.*, [3,] **7**, 554: Three grams of the material are heated in a water-bath during one hour with 100 cc. of ten per cent. nitric acid, filled to 200 cc. and polarized. The readings are calculated to dextrose.

3. A modification of the preceding: Three grams of material are heated in the water-bath with 100 cc. of a saturated solution of oxalic acid during one hour, the object being to bring the starch into solution. The liquid is cooled and filled to 200 cc. with ten per cent. nitric acid, filtered, and the filtrate heated in the water-bath one hour, attached to an inverted condenser. The solution is then polarized. This method is preferable to the other in that the cellulose and other insoluble substances are removed from the influence of the nitric acid.

4. Inversion of the starch by salicylic acid and polarization, proposed by A. Baudry, *Zeit. f. Spiritus Industrie*, **15**, 41, 42: A normal weight, 5.376 grams is adopted for the Laurent polariscope. This weight, or some multiple of it, is placed in a 200 cc. flask with 100 cc. of water and four-tenths to one-half gram of salicylic acid and heated in a water-bath for thirty minutes; fill to within twenty cc. of the mark with hot water, cool rapidly, clarify by adding a few drops of ammonia, filter and polarize in a 400 mm. tube. The readings on the percentage scale indicate percentages. In our practice, sodium hydroxide was used instead of ammonia for clarifying.

5. Precipitation of the starch from the condition of paste by barium hydroxide, and determination of the excess of the latter by titration with a standard acid, proposed by A. von Asboth, in 1887: One gram of the material, from which the fat has been extracted, is boiled with water to convert the starch into a paste; twenty-five cc. of a solution of barium hydroxide of known strength is run in and the whole allowed to cool; then add 100 cc. of eighty-five per cent. alcohol and fill to 200 cc. A compound of starch is formed containing 19.1 per cent. of barium oxide, which is precipitated by the dilute alcohol. The solution is fil-

tered and the excess of barium hydroxide is determined by titrating aliquot portions with standardized hydrochloric acid, using phenolphthalein as an indicator.

The materials to which these methods were applied included nine different samples, as follows: Pure potato starch, wheat bran, wheat middlings, wheat flour, dried potatoes, corn-meal, hay, cottonseed-meal, and a mixture of starch, sugar, and dextrine. Four of these were samples sent out by the reporter on feeding stuffs of the Association of Official Agricultural Chemists. Before examination, the samples were extracted with water and ether to remove soluble carbohydrates and fats.

The results obtained are best shown by tabulation, as follows:

Materials.	Inversion by HCl.	Inversion by HNO_3.	Inversion by oxalic acid and HNO_3.	Solution by salicylic acid.	Precipitation by $Ba(OH)_2$.
1. Pure potato starch	85.75	85.50	85.75	85.47	85.58
2. Dried potato	70.92	69.79	68.53	....	64.25
3. Wheat flour	77.69	70.65	65.29	69.38	59.76
4. Corn-meal	73.24	66.81	70.55	....	62.11
5. Wheat bran	65.86	40.25	38.68	....	70.77
6. Hay	3.48	19.10	19.10	....	66.47
7. Wheat middlings	30.00	63.09	60.24	....	60.44
8. Cottonseed-meal	4.15	....*	....*	....	54.65
9. Mixture of starch, sugar, and dextrine	9.58	21.00	24.08	18.8	33.99

* These solutions were laevorotatory.

From a survey of these data it appears that any of the methods employed, give satisfactory results when dealing with starch alone. It is important to recognize this in order that the responsibility for the discrepancies in connection with the other materials may be properly placed where it belongs; *viz.*, that the variations are due to the complex nature of the materials and not to the method. Allowing for moisture and cellulose, the starch was pure and each method gave credit for the entire amount present. Turning to the other materials the following is to be noted.

1. Inversion by hydrochloric acid. The starch is converted into dextrose and under carefully controlled conditions the reaction is quantitative. Wohl has shown that a very small quantity of acid is efficient in producing complete inversion.

(*Ber. d. chem. Ges.*, **23**, 2084.) According to Märcker, the method of Sachsse here employed gives slightly low results owing to a slight destruction of dextrose by long heating with the acid. This objection does not appear here in comparison with the other methods. There is undoubtedly danger in the other extreme in not heating long enough. The samples numbered 6, 7, 8 and 9 were treated according to the directions sent out by the A. O. A. C. which call for the removal of heat as soon as the starch-iodine reaction disappears. It is possible that under these conditions which are accomplished in a very short time, an appreciable amount of starch does not pass beyond the dextrine stage and escapes detection by Fehling's solution. In this connection it is noticeable that the samples 6, 7, 8 and 9 treated in this way, gave lower results by this than by the other methods.

2. The methods calling for the use of nitric acid seem unusually destructive, yet in the case of pure starch they have given results fairly comparable with the others. As originally proposed by the author, it was feared that the cellulose would be attacked, and the use of oxalic acid as in the third method was proposed. This provides for the solution and removal of the starch by a comparatively mild reagent and this solution is then inverted by the nitric acid apart from the accompanying constituents of the material. The method has a certain advantage of ease and rapidity; the solutions obtained for polarization are also beautifully clear and admit of accurate readings. The effect of the direct action of the acid in the second method is not so marked as might be expected.

3. Both salicylic and benzoic acids completely dissolve starch; the solutions have a right-handed polarization and the degree of rotation is directly proportional to the amount of starch present. The method was originally proposed for the valuation of commercial starches and with such materials is fairly accurate. With feeding stuffs, however, the resulting solutions are frequently too highly colored and opaque to admit of examination in the polarimeter. The method is therefore of very limited application.

5. The use of barium hydroxide as a means of combining and

precipitating starch from solution has attractive features and has been both highly praised and severely criticised. It necessitates the previous removal of all oils from the material. In our hands the results obtained have been somewhat erratic.

One fact is apparent in connection with the above data, if we leave out of consideration the pure starch sample. The results are more or less discordant and in some cases quite unexplainable. For instance, the hay and cottonseed-meal when boiled with water, do not give the iodine reaction for starch, yet each of these special methods for the determination of starch credit them with from four to sixty per cent. of the same. Even fifteen minutes warming with very dilute hydrochloric acid gives an appreciable amount of what we are bound to interpret as starch. This brings us to the inevitable conclusion, that other bodies than starch are present and respond toward each of these reactions in the same way as starch does. We know moreover that the pentosans are such bodies and that they are invariably present to a greater or less degree in materials of the kind under examination.

In order to obtain some experimental data bearing upon the subject, portions of an isolated sample of pentosans were subjected to each of the methods under discussion. The material was, properly speaking, *xylan*, since on inversion it yields only xylose. It was obtained from wheat straw by boiling the same with lime-water and precipitating the xylan with alcohol. It possessed as high a grade of purity as has thus far been attainable in the preparation of these materials. It was free from any other form of carbohydrate and contained about six per cent. of ash materials.

One gram of xylan heated for thirty minutes with fifty cc. of water and four cc. of strong hydrochloric acid was entirely dissolved. The solution was neutralized and made up to 100 cc. Of this 6.7 cc. were required to reduce the copper from ten cc. of Fehling's solution, a result equivalent to 67.16 per cent. of starch.

One gram of xylan was heated with fifty cc. of ten per cent. nitric acid for one hour and became completely dissolved. The solution was made up to 100 cc. and polarized. The reading

was equivalent to that produced by 44.73 per cent. of starch.

One gram of xylan was treated with fifty cc. of a concentrated solution of oxalic acid for one hour by which it became completely dissolved, made up to 100 cc. with ten per cent. nitric acid and heated another hour. The polariscope readings were the same as in the previous case, equivalent to 44.73 per cent. starch.

The salicylic acid method was not applicable.

One gram of xylan was boiled with thirty cc. of water, twenty-five cc. of barium hydroxide solution was added and afterwards thirty-five cc. of eighty-five per cent. alcohol and the whole made up to 100 cc. with water. Upon titration of the excess of barium hydroxide, an equivalent of 47.48 per cent. of starch was indicated.

These results show conclusively that the pentosan which is most characteristic of feeding stuffs and which has been shown to occur in all such materials, behaves, towards the reagents named, in precisely the same manner as starch and in a no less-marked degree. The conclusion is unavoidable that none of the methods for determining starch, based upon the above principles, can be employed with any degree of accuracy upon grains or forage plants or any materials where the presence of these pentosans is probable.

The most hopeful way of avoiding these difficulties would seem to be some method of bringing the starch into solution and removing it from its accompanying carbohydrates without any corresponding influence upon them. One method seems to offer this advantage; *viz.*, the application of diastase or malt infusion to the starch containing material. This method is recommended for use among the European Experiment Stations; it has been shown to yield accurate results with pure starch and can be objected to, if at all, only on account of length of time required and the difficulty of always having a proper preparation of diastase or malt infusion at hand. These are, however, minor objections in the light of greater accuracy secured. The general features of the method are as follows: The weighed material is boiled with water (most effectively under pressure) to convert the starch into a paste; after cooling to 65° C. a small quantity of malt

infusion is added and the temperature maintained at 60° to 65° for a half hour. The starch reaction having disappeared the solution may be filtered off washing the residue thoroughly, the filtrate warmed with a few cc. of acid to complete the conversion into dextrose and finally neutralized, made up to definite volume, and titrated. It remains to be seen what the effect of this process may be upon the pentosans or other similar bodies, concerning which there are few data at hand. I have made some preliminary tests which indicate that these bodies are not affected by diastase. One gram of the xylan, already mentioned, after boiling with water received ten cc. of a fairly strong infusion of malt and was kept at 65° C. for a half hour. At the same time a sample of starch was boiled to a paste, and treated with the malt infusion in the same way. The starch reaction disappeared and the solution reduced Fehling's solution strongly but the xylan did not change the Fehling's solution in the least nor did it appear to have been altered.

It seems, therefore, that in this last method the difficulties presented by the more common methods are to be avoided. The ordinary inversion methods on the other hand furnish no accurate conclusion when applied to the determination of starch contained in vegetable tissues.

For assistance in much of the analytical work cited I am indebted to Mr. D. B. Hoffmann.

NOTES ON THE HARDENING OF MORTAR.[1]

By Wm. P. Mason.

THE following is extracted from the graduating thesis of Mr. J. A. McPherson, of the class of 1894, Rensselaer Polytechnic Institute, the work having been done in my department:

It is common belief among builders, that it is better practice to mix lime mortar and let it lie in a heap some days previous to use, rather than to employ it directly after preparation. In order to test this point, samples of mortar were taken, on successive days, from two separate heaps, of large size; briquettes were made therefrom, and, after an interval of some weeks, were broken for estimation of tensile strength with the following results:

[1] Read at the Brooklyn Meeting, August 16, 1894.

	Days in heap after mixing.	Days exposed to air as a briquette.	Average breaking weight in pounds per square inch.
Mortar No. 1.....	3	50	34.6
" "	4	49	38.6
" "	6	48	38.1
" "	7	46	39.3
Mortar No. 2.....	4	48	36.0
" "	5	47	38.0
" "	6	46	41.2
" "	7	45	41.5

As concerning the formation of calcium silicate through the action of the lime upon the sand, the amount of such formation was found exceedingly small, even after great intervals of time.

After extended experiments with mortar taken from the old Van Rensselaer mansion at Albany, built about 1760, and with mortar from a very ancient tower in the valley of the Lahn, the quantity of calcium silicate found therein was 0.34 per cent. of the total weight of the mortar, an amount altogether too small to be considered as a factor in the hardening of the mortar.

The influence of tempering hydraulic mortar with water containing sugar (one-half pound of sugar to one gallon of water) is shown by the following averages, the mortar used having a tensile strength when tempered with pure water of sixty-three pounds per square inch.

Average tensile strength of sugared briquettes exposed to water during thirty-eight days was 62.75 pounds.

Similar briquettes exposed to air during same period was 65.4 pounds.

There is, therefore, a gain of three and eight-tenths per cent. over the water-tempered mortar in cases where the mortar is used in air, but no advantage when the mortar is intended for subaqueous work.

In South America there has been occasional use of bullocks' blood for tempering hydraulic mortar. In view of this, a number of experiments were made with the same mortar which was used in the sugar experiments, but the tempering was made

with bullocks' blood diluted with one-third its volume of water. The resulting briquettes set somewhat more quickly, and were very hard and firm. Their average tensile strength was:

After exposure to water during thirty-seven days, 68.3 pounds.
" " " air " " " " 69.8 "

Thus showing a gain over the water-tempering of ten per cent. for the briquettes set in air.

RENSSELAER POLYTECHNIC INSTITUTE,
June, 1894.

SOME ALLOYS OF IRON WITH MOLYBDENUM, TUNGSTEN AND CHROMIUM AS SOLUTIONS.

BY JAMES S. DE BENNEVILLE.
Received September 19, 1894.

THE results obtained by the action of silver nitrate on a ferro-tungsten of markedly heterogeneous character appeared to make a study of the reactions of the alloys of iron with the sixth family of interest. In the former paper[1] it was indicated, that a connection existed between the combining ratio of the two constituents and the chemical action of the compound toward reagents. The probable high valency of the iron atom in these metallic compounds, indicated by the fact that all that element appeared to be in combination with the tungsten; the chemical stability of the alloy and the very marked influence of the constituent tungsten on the compounds were noted, as also the nature of the alloy regarded as a solution. The work involved in the present paper is an attempt to broaden the scale of this previous investigation of one compound of a very interesting series. Alloys of the ferro compounds with the tungsten group were examined. The physical properties of these compounds as influencing their chemical properties were noted and the compounds analyzed and their quantitative composition established. The action of the weak solvent, silver nitrate, has been determined as also the reactions of the alloys with liquid and fused solvents. The discussion of the results obtained and their application to these alloys as solutions involved a short summary of the opinions expressed by others on valency and the nature of solution and the intimate connection between that state of matter and alloys.

[1] This JOURNAL, May, 1894.

The alloys were prepared by melting down cast iron with the metals at a white heat in a small Fletcher furnace working with a blast. One hour after reaching a white heat, the cast iron took up the quantity of the second metal indicated in the analyses. The melts were completely liquid and when cold were obtained in the form of buttons weighing twenty-five to thirty grams. The alloys investigated were ferro-molybdenum, ferro-tungsten and ferro-chromium.

FERRO-MOLYBDENUM.

Unalloyed molybdenum is practically infusible in furnaces working with blast. The metal probably could be obtained as a melt in the electric furnace as used by Moissan[1] in his investigations on the reduction by carbon of refractory oxides. As with many other metals of high melting-point, however, its alloys with the more fusible metals can be obtained at a much lower temperature. So with these iron compounds.

The information on these alloys is mainly due to Berthier and Thompson. Berthier states that molybdenum iron alloys are analogous to those with tungsten, a two per cent. molybdenum iron being fusible, very hard, brittle, but tenacious. Billings found that with one per cent. molybdenum, iron became red-short and worthless.[2] Thompson found that iron alloyed with molybdenum more readily than with any other metal. With equal parts of iron and molybdenum the alloy was fusible with the blowpipe. With thirty-three per cent. iron and sixty-seven per cent. molybdenum an alloy of a clear gray-white color was obtained. Twenty per cent. molybdenum iron was whiter than iron, very hard, brittle, tenacious, with granular fracture.[3]

The method of experiment followed was the use of the weak solvent silver nitrate to separate unstable alloys or the metals themselves from the more stable compounds. With the exception of chromium the elements under discussion all react with solution of the silver salt. Dr. Edgar F. Smith has shown[4] that the reaction between metallic molybdenum and the silver

[1] Since this paper was written Mr. Moissan has reduced molybdenum in his electric furnace obtaining the metal as a melt, *i. e.*, fused mass. See *Bull. Soc. Chim.*, [3], 11, 857—5 Sept., *1894*.

[2] Howe, Metallurgy of Steel, p. 86.

[3] Hiorns, Mixed Metals, p. 359.

[4] *Ztschr. anorg. Chem.*, 1, 360.

salt is very exact, silver being reduced to metal and molybdic acid formed. The ratio being Mo : 6Ag. With these iron alloys, the reaction is very complex owing to secondary reactions. The molybdenum is converted into the lower oxide of a blue color. On digesting with the neutral silver salt, no white precipitate of molybdic acid separates.

Separate portions of the alloys were crushed in a steel mortar and passed through a sixty mesh sieve. Weighed portions were then digested with excess of solution of silver nitrate. After twenty-four hours these solutions were decanted and the residue washed by decantation with water. The residue from treatment with neutral silver salt was digested with ammonia. This solution was filtered and added to the first and iron and molybdenum determined. The final residue was treated with nitric acid and, after removal of the silver, molybdenum and iron determined. By this method were obtained: 1. Iron replacing silver. 2. Molybdenum replacing silver. 3. Iron and molybdenum in stable combination.

The quantity of iron extracted by hydrochloric acid was determined. The alloys were not completely decomposed by the acid. A considerable portion of the iron was attacked but the molybdenum would be acted on only to a small extent and would appear in any ratio calculated between total iron and total molybdenum found in the residue. This did not afford a method of separating alloys soluble in the acid solvent.

The experimental results tabulated gave:

Alloy A. Nos. 1–4, close grained crystalline mass showing under the glass segregations marked by a slight yellowish tinge. This sample was fused to a clear button. Brittle, hardness 7, scratching quartz but not topaz. Fracture granular, of a silver-white color, gradually assuming, on exposure to air, a yellowish and in places a brownish tint. Strongly magnetic, not malleable, sp. gr. 8.182.

Alloy B. Nos. 5–12, appearance as with alloy A. strongly magnetic, somewhat malleable,[1] brittle, hardness seven, not so readily oxidized on exposure of fresh fracture to the atmosphere, sp. gr. 7.830

[1] Used relatively. Flattened slightly before crushing.

These alloys slowly decompose water on boiling. The terms "free" iron and "free" molybdenum are used to indicate the iron and molybdenum replacing silver in the silver nitrate. "Free" is used in the same sense throughout the remaining experiments.

I. MOLYBDENUM ALLOYS WITH SILVER NITRATE, CALCULATED TO ONE GRAM.

No.	A. Total Fe.	B. Total Mo.	C. "Free" Fe.	D. "Free" Mo.	E. Residual Fe.	F. Residual Mo.	G Ratios A : B	E : F
1 ...	0.6710	0.3290	0.3638	0.0666	0.3072	0.2624	3.50 : 1	2 : 1
2 ...	0.7106	0.2894	0.2608	0.1250	0.4498	0.1644	4.22 : 1	4.70 : 1
3 ...	0.6694	0.3306	0.2162	0.0487	0.4532	0.2819	3.47 : 1	2.75 : 1
4 ...	0.7084	0.2916	0.4932	0.1728	0.2152	0.1188	4.16 : 1	3.15 : 1
5 ...	0.8703	0.1297	0.7185	0.0666	0.1529	0.0620	11.50 : 1	4.23 : 1
6 ...	0.8893	0.1107	0.7154	0.0682	0.1529	0.0635	13.80 : 1	4.13 : 1
7 ...	0.8584	0.1416	0.5706	0.0775	0.2879	0.0640	10.40 : 1	7.73 : 1
8 ...	0.8104	0.1896	0.5328	0.1344	0.2776	0.0552	7.30 : 1	8.63 : 1
9 ...	0.7882	0.2118	0.4634	0.1260	0.3248	0.0858	6.40 : 1	6.40 : 1
10...	0.6670	0.3330	0.4939	0.1612	0.1731	0.1718	3.43 : 1	1.73 : 1
11...	0.8414	0.1586	0.4832	0.0777	0.3582	0.0809	9.10 : 1	7.62 : 1
12...	0.8883	0.1117	0.5406	0.0574	0.3478	0.0542	13.70 : 1	11.10 : 1

Taken for analysis 0.20–0.25 gram.

II. MOLYBDENUM ALLOYS WITH HYDROCHLORIC ACID, CALCULATED TO ONE GRAM.

No.	A—13.	B—14.
Iron	0.5982	0.6933
Per cent. of total iron	86.74	83.86

Taken for analysis, two grams.

III. MOLYBDENUM ALLOYS, CARBON, SILICON, PHOSPHORUS.

No.	Sample.	Total C, per cent.	Combined C, per cent.	Graphitic C, per cent.	Si, per cent.	P, per cent.
15.....	Pig iron[1]	2.99	0.37	2.62	2.92	0.33
16.....	Alloy A	2.90	0.17	2.73	0.74	0.31
17.....	Alloy B	2.97	0.20	2.77	0.66	0.30

A third sample was obtained by melting cast iron in the presence of twice its weight of molybdenum. At the heat obtained this was fused down to an irregular mass but a clean button was not obtained. It was very crystalline in structure, the luster in places being of the nature of "parrot" copper ore. The portion unattacked by the weak solvent is of interest, the remainder evidently containing unalloyed molybdenum. The "residual" iron and molybdenum obtained, gave:

[1] Sp. gr., 6.980.

IV. MOLYBDENUM ALLOYS, C.

No.	Residual Fe.	Residual Mo.	Ratio.
18	0.7394	0.2606	4.85 : 1
19	0.4267	0.5733	1.40 : 1
20	0.1320	0.8680	1 : 5
21	0.0770	0.9230	1 : 7

By HCl 42.63 per cent. of total iron dissolved.

In table I the analyses appear to show that the silver nitrate acts not only on unstable alloys but on iron as such or on molybdenum as such. The attacked and unattacked portion varies considerably through the mass. Table IV indicates the influence of mass action. The quantity taken for experiment (0.20–0.25 gram) was small and any marked differentiation would appear. If iron be regarded as limited in its lower compounds by divalency the formula Fe_3Mo (molybdenum being regarded as hexavalent) would represent the saturation-point corresponding to 63.64 per cent. iron and 36.36 per cent. molybdenum. If now the alloy contain less molybdenum than thirty-six per cent., either: 1. The iron in excess must be regarded as present as such in the same sense that water in excess is present in an unsaturated solution, or 2, the alloy is analogous to a cryohydrate, there being present a definite compound or compounds and the excess of the solvent, forming one homogeneous system in its liquid and melted condition, but in the solid (*i. e.* frozen) form making up a system in which the parts bear a definite relation to each other as in cryohydrates, or in which the excess of the solvent is present in a form analogous to ice in such mixtures. 3. That while there may be definite compounds formed in the alloy yet the main bulk of the system is in chemical union, all the iron being united to all the molybdenum no matter how large the quantity of either constituent. 4. That in solution the iron and the molybdenum may be in combination up to the full power of their respective valencies, but that this valency is not exercised (or its power decreases) on cooling, on which the more stable forms of combination appear. Iron or molybdenum in excess may then be present in the solidified alloy and it is not unlikely that owing to the very high melting-point of molybdenum that, as the fusing-point of the mixture rises, a part of the molybdenum exists as a mechan-

ical mixture either never having been in combination with the iron or separating out from the alloy on cooling and the exercise of the more stable valency.[1] The action of a weak solvent, as of any solvent, is mainly dependent on the affinity between the constituents of the compound. That iron and molybdenum form a stable alloy is evidenced by the fact that the action of strong hydrochloric acid fails to decompose these compounds but leaves a residue more or less rich in iron. The silver nitrate can then be regarded as a solvent of a definite compound or compounds in the solidified alloy acting on these and on the metal in excess but failing to attack the more stable compound. Both iron and molybdenum react with the silver salt and the failure of this reaction to take place with considerable percentage of the alloys also points to a strong affinity between the two elements. As with tungsten this is to be expected from the nature of molybdenum as semi-metal. Increased percentage of molybdenum accompanied increased brittleness and decrease in fusibility. The alloys were decomposed by nitric acid which converted the molybdenum to molybdic acid; by potassium bisulphate with evolution of sulphurous anhydride; by fusion with mixture of sodium carbonate and saltpeter; hydrochloric acid left a residue rich in molybdenum.

Analytical Methods.—The direct analysis of these molybdenum alloys (for iron and molybdenum) can be readily made by two methods. 1. The powdered alloy can be fused with oxidizing mixture with addition of caustic soda, cooled and lixivated in water and the soluble sodium molybdate separated by filtration from the residual ferric hydroxide. The molybdenum can then be determined by neutralizing with nitric acid the whole, or an aliquot portion of the solution of alkali molybdate, using methyl-orange as an indicator, and precipitating in the neutral solution as lead molybdate according to Chatard's method.[2] 2. A convenient method of analysis was found by solution in nitric acid. Excess of acid is removed by evaporation and excess of ammonia and ammonium sulphide is then added, digesting in a warm place for at least an hour and acidifying with hydrochloric acid and boil-

[1] Lothar Meyer, Modern Theories of Chemistry, pp. 307, 308.
[2] Fresenius, Quantitative Analysis, p. 353.

ing. Hydrogen sulphide is then passed through the hot solution until saturation. In the indirect analysis (with silver nitrate), after removing silver by hydrochloric acid, it was found necessary to oxidize the boiling solution by nitric acid otherwise the molybdenum remains partly in the form of the lower oxide which does not appear to be readily converted to sulphosalt and on dissolving the iron sulphide in hydrochloric acid the blue color indicates the molybdenum in solution. The precipitated molybdenum trisulphide is oxidized by nitric acid, filtered from any residual sulphur and the cold acid solution precipitated by barium nitrate avoiding an excess. The barium sulphate is filtered off, the filtrate neutralized by ammonia, leaving it barely but distinctly acid, and the molybdenum precipitated as lead molybdate. Throughout these analyses iron is determined volumetrically in sulphuric acid solution by titration with permanganate. A very pure zinc was used for reduction.

Table III explains itself. There appears a decided decrease in the percentage of silicon and a slight increase in the graphitic carbon over the combined. The phosphorus shows no change. The two analyses are only suggestive not indicative of these differences as due to the molybdenum. In determining both phosphorus and silicon the formation of phospho- and silico-molybdate,[1] at least partly soluble, must be taken into account. The graphitic carbon is that determined after treating the iron with hydrochloric acid. In ordinary steels the combined carbon is readily decomposed by the acid and the residue in these irons is probably free from combined carbon. Combustion of the powdered alloy only gave partial results. These alloys slowly decompose water on boiling. Their heterogeneity was apparent on so treating fragments of the alloys, brownish and yellowish spots due to oxidation being scattered over the exposed surface. These were distinct from the iron rust which was also formed. Metallic molybdenum decomposes water on boiling. The richer the alloy in molybdenum the more readily it decomposes water.

FERRO-TUNGSTEN.

The experiments in a former paper[2] on ferro-tungsten were

[1] See under ferro-tungsten.

[2] This JOURNAL, May, 1894.

made on an alloy containing, on averaging twelve analyses, 53 per cent. iron and 46.3 per cent. tungsten and of 10.14 sp. gr.[1] A second alloy of eighteen per cent. tungsten was made. The method of preparation and experimentation followed was the same as with the molybdenum compounds. The action of tungsten on silver nitrate has been found by Smith[2] to be analogous to that of molybdenum. Tungstic acid is formed and silver reduced to metal, the ratio being W : 6Ag.

In the alloy previously described (Nos. 22–26) it was found that the iron and tungsten were present in a very stable form, only a small percentage of tungsten and iron being attacked by the silver solution. In view of the more extended experiments this soluble portion can be regarded as a part of the alloy more readily attacked than the residue. Schneider separated from a high tungsten iron what appeared to be two alloys, one magnetic and the other non-magnetic corresponding to the formulas Fe_3W and Fe_8W. He used hydrochloric acid as a means of separation from the soluble iron.[3] It must be taken into consideration, however, that tungsten is but little attacked by hydrochloric acid and in the case of an alloy of which the iron was readily attacked by acid it would be left in the residue and vitiate any ratio calculated from analysis of that residue. With silver nitrate, however, there is a definite reaction between the silver and the constituents of the alloy. They both act on it, although (and the varying ratios point to the latter alternative) the doubt exists as to whether the silver salt attacks a definite compound or varying quantities of alloys of different composition. The chemical inertness of these alloys is much more conspicuous than with the molybdenum compounds. Whatever compounds are formed in these alloys, are probably compounds made up of atomic linking and not the union of like molecules. These compounds are formed from a solution, and Heycock and Neville on determining the molecular weights of metals dissolved in sodium found for copper, silver, lead, antimony, zinc, cadmium and mercury, one atom in the molecule. Ramsay obtained like results by

[1] I am indebted to Dr. Wm. H. Wahl through Mr. F. Lynwood Garrison for this alloy.

[2] I am indebted to Dr. Smith in a private communication for reactions of molybdenum and tungsten bearing on these alloys. See *Ztschr. anorg. Chem.*, 1, 360.

[3] Howe, Metallurgy of Steel, p. 81.

determination of the variation of vapor tension of mercury.[1]

Analytical Methods.—The best method for direct analysis of these compounds was found to be fusion with the oxidizing mixture with addition of caustic soda and lixiviation in water. The soluble sodium tungstate was filtered from the residual ferric hydroxide and the tungsten precipitated in neutral solution by mercurous nitrate according to the method of Wolcott Gibbs.[2] In the indirect analysis, to the solution obtained on filtering from the unattacked residue, ammonia in excess was added and then ammonium sulphide. After digesting in a warm place for an hour this solution was acidified by hydrochloric acid and boiled. Hydrogen sulphide was then passed through it to saturation and the precipitate of silver sulphide and tungsten trisulphide filtered off and tungsten separated from silver by solution in ammonium sulphide. After removal of ammonium salts and oxidation, tungsten was determined as tungstic oxide, WO_3. The unattacked residue, after removal of silver,[3] was fused with oxidizing mixture and the sodium tungstate separated from the residual ferric hydroxide by lixiviation in water and filtration.

The experimental results gave:

Alloy D, Nos. 22–26.[4] Crystalline with marked differentiation throughout the mass showing a number of cleavage planes of a pyritous appearance, also lining the cavities. The body or cementing portion of the alloy being finely crystalline but without the luster of the molybdenum compounds. Hard, brittle and tough. Sp. gr. 10.14. Alloy E, Nos. 26–29. Fine-grained crystalline mass without visible differentiation. Color, dark gray, the original pig iron being lighter in color. Brittle. Hardness barely 7. Sp. gr. 7.935. This alloy scratched glass readily; quartz only with difficulty. On boiling in water and subsequent oxidation this alloy showed patches of brown, yellow and bluish spots distinct from the iron "rust" formed.

[1] Mendelejeff, Principles of Chemistry, 1, 123. Ramsay obtained with barium, calcium, and potassium abnormal results, the number representing the first two metals being one-half the atomic weights. With potassium a number considerably less than its atomic weight was obtained.—*J. Chem. Soc. Trans.*, *1889*, 521.

[2] Blair, Chemical Analysis of Iron, p. 123. Modified as described in Classen (trans. of Smith) p. 174.

[3] This residue was not attacked by dilute nitric acid.

[4] As described by Dr. Wahl.

These oxidation-points were distributed all through the mass with considerable uniformity.

V. TUNGSTEN ALLOYS WITH SILVER NITRATE, CALCULATED TO ONE GRAM.

No.	A. Total Fe.	B. Total W.	C. "Free" Fe.	D. "Free" W.	E. Residual Fe.	F. Residual W.	G. Ratios A : B.	G. Ratios E : F.
22..	0.5166	0.4834	0.0122	0.0403	0.5044	0.4431	3.51 : 1	3.74 : 1
23..	0.4109	0.5891	0.0283	0.0526	0.3826	0.5365	2.30 : 1	2.34 : 1
24..	0.5276	0.4724	0.0566	0.0370	0.4709	0.4355	3.66 : 1	3.54 : 1
25..	0.5270	0.4730	0.3156	0.0632	0.2093	0.5881	3.66 : 1	1.17 : 1
26..	0.5265	0.4735	0.0152	0.0541	0.5096	0.4211	3.66 : 1	4 : 1
27..	0.8053	0.1947	0.7104	0.0652	0.0949	0.1295	13.6 : 1	4.17 : 1
28..	0.8119	0.1881	0.7111	0.0760	0.1008	0.1121	14.1 : 1	3.4 : 1
29..	0.8124	0.1876	0.6980	0.0721	0.1144	0.1155	14.2 : 1	3.15 : 1
30..	0.8584	0.1416	0.7393	0.0331	0.1221	0.1055	20 : 1	2.6 : 1

Taken for analysis, 0.20–0.25 gram.

VI. TUNGSTEN ALLOYS WITH HYDROCHLORIC ACID, CALCULATED TO ONE GRAM.

No.	D–31.	E–32.
Iron	0.3728	0.6223
Per cent. of total iron	70.34	75.70

Taken for analysis, two grams.

VII. TUNGSTEN ALLOYS, CARBON, SILICON, PHOSPHORUS.

No.	Sample.	Total C, per cent.	Combined C, per cent.	Graphitic C, per cent.	Si, per cent.	P, per cent.
33.....	Alloy D[1]	2.40	1.84	0.56	2.07	0.25
34.....	Pig iron[2]	3.06	0.77	2.29	3.30	0.32

These alloys also are marked by heterogeneity, containing more and less stable compounds. Their crystalline character is more prominent than with the molybdenum compounds, cavities in the alloys being lined with imperfect crystals by no means microscopic and showing cleavage planes of a pyritous appearance. Poleck and Grützner[3] have examined one of these forms in a ferro-tungsten. Their description of the alloy is of a crystalline mass, dense and hard, of a steelish gray color, metallic luster, with cavities lined with small crystals, found by Hintze to be of the hexagonal system or possibly rhombohedral if hemihedral in form. They were nearly as hard as corundum and were completely attacked by sodium potassium carbonate, giving the formula FeW_2 analogous to FeS_2. The cementing material

[1] Made from tungsten and pig iron, No. 34.

[2] Sp. gr., 7.146.

[3] Abstracted *Bull. Soc. Chim.*, No. 8, *1893*.

gave the formula $Fe_2W_2C_3$ and was nearly as hard as the crystals. Density 12.92–13.14. F. N. Riddle[1] smelted Lake Superior hematite with tungstic oxide and carbon. In the crystalline mass were obtained steel-gray crystals insoluble in hydrochloric acid and found to contain 98–99.5 per cent. tungsten. Density 15–16. With nickel he states the separation of this crystalline tungsten was still more marked. The variation of results among different observers shows the influence the conditions of preparation have on alloys of iron and tungsten.

The chemical reactions of these tungsten alloys strongly indicated the influence of the tungsten. Acid solvents were practically useless as a means of analysis. Both nitric acid and aqua regia decompose them but very slowly and only by removing the protecting coating, the yellow hydroxide $Wo(OH)_2$ and adding fresh acid. Potassium bisulphate (sulphuric acid at a red heat) decomposes them with evolution of sulphurous anhydride. An oxidizing mixture of sodium carbonate and saltpeter was a complete and ready means of decomposition, as also was caustic soda. Hydrochloric acid acts only partially on the iron. These reactions are those of metallic tungsten and indicate a combination of iron and tungsten equally inert.

The formation of phosphotungstate and silicotungstate, partly, at least, insoluble and remaining with the tungstic acid, necessitated some modification in the determination of these elements. The separation was made by fusing the powdered alloy with oxidizing mixture and caustic soda dissolving the melt and filtering from the residue. This residue was treated in the usual manner for silicon. To the solution containing alkali tungstate, silicate (in part), and phosphate, enough ferric chloride is added to precipitate silicic and phosphoric acid. The solution is now acidified, the ferric carbonate formed dissolving. Carbon dioxid is expelled by boiling, and ammonia in excess added to re-solution of precipitated tungstic acid. Silicic and phosphoric acids are now determined as usual. In determining arsenic and phosphorus in pig copper this method was found to be accurate, these elements going with iron in preference to lead, antimony, tin, or bismuth.[2]

[1] *Am. J. Sci., 1889*, [3], **38**, 160.

[2] Modification of a method described in Crookes' Select Chemical Methods, p. 430.

FERRO-CHROMIUM.

Since the publication in 1820 by Berthier[1] of his experiments on alloys of chromium with iron, these compounds have been carefully studied both from a chemical and physical standpoint with regard to their metallurgical application. Physically, chromium increases the hardness and tensile strength of iron, but makes it brittle. As noted in the discussion of ferro-molybdenum the properties of hardness and density appear to be connected with condensation, and in the case of both these properties they increase with the content of chromium. Brustlein[2] notes that the carbon increases with the chromium, giving a series from twelve per cent. chromium, two per cent. carbon to eighty per cent. chromium with eleven per cent. carbon. Howe[3] also notes this increase of the carbon content and also that, as in the case of manganese, the chromium prevents the separation of graphitic carbon. According to the same authority chromium combines with iron "in all proportions or at least up to eighty per cent." the alloys being markedly heterogeneous in nature, samples from the same piece giving very different results when subjected to physical tests. He etched a plate of chrome steel with sulphuric acid and noted in it the presence of portions not attacked by the acid and which he considered probably to be alloys rich in chromium. The analyses made for this paper give the same results in regard to heterogeneity in these chromium alloys and in the other alloys examined and show the necessity of taking from half to one gram of an average for analysis. The experimental method pursued was the same as with the molybdenum and tungsten alloys. Nitric acid, dilute or concentrated, does not attack metallic chromium. The silver nitrate would not, therefore, attack the chromium constituent of these alloys. The action of the reagent, however, is of interest as showing the amount of iron in stable combination and the figures so obtained are given. The chromium alloys of iron show the influence of the chromium in almost as positive a manner as with tungsten compounds. Acid solvents act very slowly on high chrome alloys. Potassium bisulphate and the oxidizing mixture decompose them

[1] *Annalès des Mines*, [1] **6**, 573.
[2] Hiorns, Mixed Metals, p. 359.
[3] Howe, Metallurgy of Steel, p. 75.

readily, and the latter energetically, the oxidation of the fine powder giving rise to a considerable evolution of heat which rapidly raises the crucible to bright redness; only one alloy was made.

Alloy F. Brilliantly crystalline; acicular, with a cleavage appearance like antimony. Brittle. Scratches glass with difficulty. Does not scratch quartz. Specific gravity, 7.464. Hydrochloric acid decomposed this alloy.

VIII. CHROMIUM ALLOY WITH SILVER NITRATE, CALCULATED TO ONE GRAM.

No.	A Total Fe.	B Total Cr.	C "Free" Fe.	D Residual Fe.	E Residual per cent. Fe.	Ratio A:B.
35.....	0.8706	0.0794	0.4832	0.3874	44.49	10:1
36.....	0.8684	0.0804	0.4497	0.4187	48.21	10:1
37.....	0.8481	0.0999	0.4770	0.3711	43.75	8:1
38.....	0.9154	0.0360	0.5092	0.4062	44.37	24:1

Taken for analysis 0.20–0.25 gram.

IX. CHROMIUM ALLOY, CARBON, SILICON, PHOSPHORUS.

No.	Sample	Total C, per cent.	Combined C, per cent.	Graphitic C, per cent.	Si, per cent.	P, per cent.
40	Alloy F.....	2.46	1.64	0.82	3.37	0.29
41	Pig iron	3.06	0.77	2.29	3.30	0.32

No. 40 was made by melting No. 41 with ninety per cent. ferrochrome.

Analytical Method.—In direct analysis for determination of chromium and iron the fusion with oxidizing mixture was adopted and separation of the chromate from ferric hydroxide effected by filtration. In determining iron and chromium digested with silver salt, the insoluble residue was dissolved in aqua regia, the silver chloride filtered off and the solution made alkaline by sodium hydroxide, boiled and bromine added. The residue of ferric hydroxide was filtered from the chromate. In the acid filtrate the chromic acid was reduced by hydrogen sulphide and the boiling solution precipitated by ammonia. Adhering alkali, forming chromate on ignition, was tested for by mercurous nitrate.[1]

GENERAL CONSIDERATIONS.

In connecting solutions and alloys the part that the metal in excess plays is that of water in aqueous solutions of salts. That

[1] A Method used for chromite analysis by Dr. F. A. Genth.

this is not a purely mechanical part but that a distinct force is acting between the components of a solution is evident from the modification both of solvent and of the dissolved substance. The physical state of the latter changes, probably assuming the liquid form,[1] and the specific gravity, refractive power, tension of vapor, boiling and freezing-points,[2] are affected often considerably. The thermic effect resulting in evolution or absorption of heat, and alteration in volume[3] shown by contraction or expansion, further indicate chemical action. The combination is an indefinite one in so far as addition of the solvent is concerned; but the amount of dissolved substance is strictly limited by temperature and pressure (in the case of gases). Van 't Hoff[4] has intimately connected gases and solutions comparing diffusion to evaporation and solution to vaporization. His experiments on osmotic pressure, showing that solutions obeyed the laws of gases and that Avogadro's law could be applied to them.

The formation of definite compounds in solution is well established, the halogen acids and nitric acid affording examples of solutions of constant boiling-point; and until that concentration is reached the products of evaporation are mainly water or, as the case may be, acid.[5] The cryohydrates are also examples of this definite combination, and such substances as $H_2SO_4H_2O$ and salts with water of crystallization. Although these very definite compounds are formed with water, solution itself is a homogeneous system[6] and the existence of these compounds as such in the fluid cannot be asserted. Sterry Hunt, who considers solution as the type of chemical action in its "identification of the different," regards the state as one in which all definiteness is lost and in which we cannot assert the existence of any one compound, or even element, more than another.[7] We can only possibly predict what, under altered conditions, we can obtain from it.[8] He sums up the theory of solution as "the formation of

[1] Mendelejeff, Principles of Chemistry, 1, 70.

[2] Ibid, 1, 86, 87.

[3] Lothar Meyer, Modern Theories of Chemistry, 466, 481.

[4] *Trans. Swedish Acad. Sciences*, Part 21, No. 17, *1886*; quoted by Mendelejeff, 1, 64, 65. See translation by Ramsay, *Phil. Mag.*, 26, 81, *1888*, from *Ztschr. phys. Chem.*

[5] Ostwald, Solutions, p. 9, trans. by Muir.

[6] Ibid, p. 148.

[7] New Basis of Chemistry, p. 22. [8] Ibid, p. 10.

definite compounds with water accompanied with all the phenomena of chemical union," further addition of water giving rise either to decomposition and formation of new compounds or to admixture of "one definite solution or liquid species with another less dense solution, or with water." These compounds "being separable in a solid state by change of temperature or in a liquid state (theoretically) by gravity;" liquidity is but an accident of solution, depending on temperature and pressure.[1] Arrhenius from his investigations of the depression of the freezing-points and lowering of the vapor pressure of solutions of electrolytes came to the conclusion that the system was one of dissociation.[2] Mendelejeff bringing all such compounds as solutions, cryohydrates, colloids, and amorphous silicates, under the law of definite and multiple proportions regards solutions as fluid unstable definite chemical compounds in a state of dissociation.[3]

Alloys, with the exception of some of the amalgams, are solids at the ordinary temperature and require a more or less elevated degree of heat for fusion, their melting-point depending on that of their constituents and on the nature of the alloy. As solutions, therefore, they only exist at high temperatures and it is at those temperatures that the laws of solutions must be applied to them. As is the case with liquids, they may be saturated or unsaturated compounds, in the latter case one of the constituents being present in excess and acting as the solvent, *i. e.*, corresponding to the part excess of water plays in the solution of a salt. If the solution be regarded as a state of dissociation, then while the mass of the alloy is in the liquid state (fused) we have a homogeneous system, and two elements may be in unstable combination which on cooling, *i. e.*, solidifying or freezing, separate in definite compounds limited by the valency of the constituents, any excess of one of the elements being indicated by the presence of that element in an uncombined state. When, therefore, there is no excess indicated in an alloy of one constituent over another it can be justly assumed that all is in combination, and the presence of an excess of one of the metals

[1] Systematic Mineralogy, pp. 77, 78, 82.
[2] Ostwald, Solutions, pp. 189, 214. Trans. of Muir.
[3] Mendelejeff, Principles of Chemistry, I, 105.

would correspond to the ice present when an aqueous solution of a salt is cooled below its freezing-point, or to those compounds of salts with much water known as cryohydrates. The freezing-points of metals and their alloys, with a few exceptions, are much higher than the normal temperature, 15° C. In his study of the solution of liquids in liquids W. T. Alexeef found that two liquids mutually soluble, intermix in all proportions at certain temperatures. At lower temperatures the solubility is limited, finally reaching a minimum.[1] This may be and probably is the case with melted metals, but the condition in which we can observe and examine them corresponds, as said before, to the frozen state.[2] Hardness and indifference to chemical reagents have long been associated with condensation, increased density being generally associated with these properties and indicating complexity of structure advancing from the gaseous to the solid form.[3] In liquids, although friction appears as a factor, yet there is free communication within the bounds of the liquid; a considerable condensation, however, takes place. In the conversion of steam, gaseous H_2O, to water and ice, Sterry Hunt found this condensation to be for water, 1192 H_2O, and for ice, 1094 H_2O,[4] and in mineral species increased density was found to be associated with hardness and chemical indifference.[5] Ramsay in determining the molecular formulas of liquids by means of their molecular surface energy, found that condensation increased with fall in temperature and obtained for sulphuric acid of 1.82 sp. gr. the very complex formula not lower than $(H_2SO_4)_{22}$ at ordinary temperatures.[6]

Regarding alloys as solutions, many of their physical properties can be explained. The alloy changes its nature both physical and chemical, differing from its constituents in volume (*i. e.* density) and melting-point, and forming often definite molecular compounds. This modification of its properties is greater or

[1] Mendelejeff, Principles of Chemistry, 1, 74, and Ostwald, Solutions, p. 40, trans. of Muir.

[2] Ibid, 1, 105.

[3] Sterry Hunt, Systematic Mineralogy, p. 86, seq.

[4] New Basis of Chemistry, p. 109.

[5] Researches of J. B. Mackintosh, *J. Anal. Chem.*, 1, 10. Sterry Hunt, Systematic Mineralogy, p. 93.

[6] *J. Chem. Soc.*, **63**, 1089, Sept. *1893*. **65**, 167, March, *1894*.

less according as the constituents are separated in their nature. Mendelejeff cites the series formed by sodium with chlorine, sulphur, phosphorus, arsenic, antimony, tin, and zinc, changing its properties from the distinctly saline sodium chloride to the sodium zincide and with this change in properties as the union is with the element more and more like in nature to sodium increasing in valency; but they are distinct and definite compounds and not to be distinguished on the ground of chemical nature. He notes the same properties in the union of metallic oxides, instancing the large number of complex aluminum silicates in which the two constituents are very like in nature acting as feeble base or feeble acid, and united in such a substance as lava glass in varied proportions giving on crystallization definite compounds, the silicates.[1] The analogy between these vitreous substances, with their microcrystalline structure, and alloys is a striking one.

The question of variable valency of the elements arises in these compounds of like elements. Are they to be regarded in the same light as with those of rigidly defined proportions with unlike elements? This is evidently the case. Definite crystallized compounds of alloys are known, with well-defined properties unlike those of either of the constituents. The alloys $SnCu_3$ and $SnCu_4$, as also $PbSn_3$, are examples. Polymerism has also its analogue in allotropism.[2] But in the union between unlike elements this variability appears. Sodium forms several oxides, as likewise gold, silver, copper, etc. The elements under consideration, chromium, molybdenum, and tungsten, unite with oxygen in several ratios. These latter are especially interesting in their relation to the silicates. The complexity of their silico-compounds and phospho-compounds, was long ago established by Wolcott Gibbs[3] and if this complexity is related to the union of like properties in these oxides the same complexity is to be expected in the union of elements of like nature—as these metals. These alloys in the melted state are solutions, as the melted lava glass is a solution. There is a homogeneous system

[1] Mendelejeff, Principles of Chemistry, 1, 111,112. See Matthiessens Conclusions, *Brit. Ass. Reports, 1867*, p. 97, cited in Fownes' Chemistry, p. 290.

[2] Ernest Meyer, History of Chemistry, pp. 377, 454.

[3] Gibbs, *Am. J. Sci.*, [3], **14**, 61.

the equilibrium of which is disturbed on cooling and at different temperatures different salts crystallize out. These salts may represent combinations of the atoms as truly as NaCl or they may be molecular compounds of a salt with the solvent metal, *i. e.*, present in definite proportion analogous to water of crystallization as in the salt $Na_2CO_3, 10H_2O$. The number of such compounds separating out during the slow cooling of an alloy may be, and probably is, very great. In many alloys with slow cooling, a macrocrystalline structure often results, but with rapid cooling the result is the microcrystalline form. This is of such importance that the commercial use of many alloys requires their rapid cooling, from their tendency to coarsely crystalline structure and consequent loss of homogeneity. That the valency of an element is related to its electro-chemical behavior has been shown and the value of an element increases toward like elements and decreases or concentrates itself in union with unlike elements, *i. e.* "Elements of variable valency exercise the smaller valency when combining with those for which they have the greater affinity but the higher valency when uniting with those for which they have but small affinity.'[1] The possibility of self-saturation must be taken into account[2] and valency established on indirect determination is doubtful. In these compounds or alloys the question of valency becomes a very difficult one. The quantitative composition of a well-developed individual, such as a crystal, is no guide in itself to the valency of the constituents as crystallization is essentially molecular. We know that the passage from gas to liquid and to solid involves a condensation and most frequently a very great condensation of volume, and experiment on the solutions of metals in mercury and in sodium show many of them to be monatomic; therefore, while the molecule itself may contain but a comparatively small number of atoms, the union of these simple molecules to form larger ones brings about great complexity of structure indicated by the increased density, hardness, and chemical inertia. If this is the case the molecule of these ferro-compounds must be very complex and assuming the simplest formulas from the

[1] Lothar Meyer, Modern Theories of Chemistry, p. 349.
[2] Ibid on valency, p. 307 seq.

analyses—which, while representing the average of a number of alloys in the solid state, can be carried back to the liquid state when the system was homogeneous—very large integral weights or equivalents are obtained. The valency of iron to tungsten is at least equal to its valency to chlorine or to oxygen, and these are only minima. Ruthenium and osmium have been shown to be at least octovalent, and if the ammonia (NH_3) in the ammonium cobalt salts be considered as atomic and not molecular, cobalt, a metal closely allied to iron, must be accepted as dodecavalent.[1] The ratios obtained in column G of the tables do not afford an indication of the value of the iron atom in these alloys. The ratio E : F of the residues give for the highest formulas $Fe_{11}Mo$ and Fe_4W, but unquestionably represent mixtures.[2] The presence of an allotropic form of iron, β iron, as taught by Prof. Osmond, is also to be taken into account. These elements of the sixth family, tungsten and chromium, come under the list of β forming elements. As far as the solution of steels in acids or in the copper alkali salt, this β or hard "adamantine" form of iron appears to act as other modifications. There is no reason to believe it would act differently with silver nitrate.[3] The influence of mass appears in the increased ratio of the predominant metal in E : F. This is not so marked in the case of tungsten. A considerable uniformity runs through the analyses but several numbers (as I, 8, 9, 10) evidently mark points of segregation.[4]

[1] Lothar Meyer, Modern Theories of Chemistry, pp. 347, 348.

[2] The silicides and phosphides of iron are very inert. A ferro-silicon containing fifteen per cent. silicon was insoluble in nitric or hydrochloric acid, but soluble in aqua regia.

[3] Prof. Osmond in his paper (*J. Iron and Steel Inst.*, p. 38, *1890*) ascribes the power of retaining at the normal temperature iron in this β or hard form, to a number of elements among them tungsten and chromium; the hardness of such iron being due not only to the mechanical strains set up in the solid on cooling but to molecular strains, perhaps due to osmotic pressure exerted by elements of small atomic volume (discussion of Prof. J. O. Arnold's paper, May, *1893*). Prof. Arnold considers the hardening property as due to mechanical strains on cooling probably caused by the formation of definite compounds such as Fe_3C. These authorities do not appear to regard as worthy of notice the theory that all the carbon, phosphorus, silicon, etc., is uniformly distributed through the iron and in combination with it; and in view of the small quantities of such elements present such a view appears chemically untenable. I am indebted to Mr. Garrison, who kindly brought these papers to my attention and placed them at my disposal for consultation.

[4] In the action of silver nitrate on these alloys there is a considerable evolution of heat. This is also the case with iron.

That the melting-point of alloys is not the mean of the melting-points of their constituents but is influenced by properties probably chemical, is well known. An example of this is afforded by platinum which is only fusible by the oxyhydrogen flame in a lime furnace, but which with iron forms a readily fusible alloy at the highest temperature of the blast-furnace and also with a number of other elements, alloys fusible at the heat of the Bunsen lamp. This lowering of temperature is found with other still more infusible elements of this group; *viz.*, palladium, iridium, ruthenium, and osmium.[1] Tungsten, molybdenum, and chromium, form a group of very infusible substances but these iron alloys are formed readily at the temperature of the blast-furnace. Hardness, chemical indifference, and density are associated with molecular complexity and the tungsten group in their metallic forms are probably represented by formulas expressing great condensation and affinity between the like atoms. The formation of these iron alloys, therefore, must be preceded by a breaking up of this union between like atoms and molecules and this is brought about by a state of solution. The affinity of iron and the sixth family is then greater than the affinity of the like atoms, for on cooling from the homogeneous system of solution stable alloys of iron and the second constituent separate out. Now, as before cited, Heycock and Neville found (confirmed by Ramsay) that on determining the molecular weights of the metals dissolved in sodium and in mercury the results gave one atom in the molecule for a large number of metals, indicating that in solution in metals, a state of dissociation exists analogous to that of the aqueous solution. If this holds good, therefore, for these iron compounds, that in the liquid or melted condition the complex molecule of iron and tungsten existing in the solid state is broken up into a simpler form, then the affinity between the constituents of these alloys can act. The investigators found that on dissolving the metals in atomic proportions in molten tin on applying Raoult's method[2] to the lowering of temperature of solidification a constant was obtained, this being in accordance with Coppet's law

[1] Howe, Metallurgy of Steel, p. 79. A. Joly., *Compt. rend.*, *1893*, **116**, 430, on melting-point of the platinum metals.

[2] See *Am. Chem. J.*, **11**, 67, 72.

that "solutions whose contents are in the ratio of the molecular weights of the dissolved salts freeze at nearly the same temperature.[1]" That is, the freezing-point is a function of the molecular weight. Indium and aluminum gave abnormal results indicating a more complex molecule in solution.

Chemical action is also indicated by change in volume and in his researches on dilute solutions Ostwald determined the amount of chemical change—in this case representing the avidity of the acids—by the contraction or expansion of the liquid.[2] With alloys, the same phenomena is observed. As a rule with the formation of definite compounds, *i. e.*, on cooling, contraction ensues. Alloys of bismuth, however, expand being analogous in this respect to ice. These iron alloys show change in volume, indicating by their increased density that with them a contraction has taken place. In every case there is a marked increase in specific gravity. Comparing the specific gravities:

X. TABLE ON COMPARATIVE DENSITIES.

Nos.	Samples.	Sp. gr. of metal.	Sp. gr. of alloy.	Composition.	Sp. gr. of pig iron.	From composition, difference.	Equivalent weights.
1–4	A.....	Mo=8.6	8.182	Fe_4Mo	6.980	+0.88	175052
5–12	B.....	.....	7.830	Fe_8Mo	6.980	+0.67	167562
22–26	D	W=19.2	10.140	Fe_7W_2	.....	.....	216996
27–30	E.....	.....	7.935	$Fe_{16}W$	7.146	+0.08	169809
35–38	F.....	Cr=6.8	7.446	$Fe_{20}Cr_3$	7.146	+0.27	159629

Fe here represents the complex compound containing phosphorus, silicon, and carbon—pig iron. The sign—minus is to be expected with chromium. If these alloys are to be considered as chemical compounds and as atoms bound together into molecules and these molecules into still more complex molecules then these composition formulas, can be taken as representing the simplest average composition of the definite compounds in the alloy in the solid state. There may be and certainly are compounds in these alloys represented by formulas more complex than these simple formulas, for the elements, carbon, silicon, etc., have not been taken into account. Assuming these latter, however, column VI gives the equivalent weights $H_2O = 21400$.

[1] *J. Chem. Soc. Trans.*, *1889*, 666, *1890*, 376. Ramsay, Ibid, *1889*, 521. Quoted in Ostwald, Solutions, p. 231, by Muir.

[2] Lothar Meyer, Modern Theories of Chemistry, p. 481 seq.

These high equivalents explain the physical properties, such as hardness and density, and the chemical inertia of these compounds.[1]

In this connection it should be noted that there is a difference in density in a metal as solid and when in the melted condition. Wrightson[2] in his experiments on the relative specific gravity of cast iron in the two states found that the maximum volume was obtained on passing from the liquid to the solid. The same result was obtained from experiments made on melting solid iron or on cooling molten iron to solid. In the latter case there was observed: first an expansion, followed by contraction and again by expansion. The observed differences were small. Henri Moissan in his experiments on carbon dissolved in iron made use of this change of volume of the iron to subject the carbon, on sudden cooling, to great pressure.[3]

From these results it can be concluded:

1. That these alloys by their resistance to chemical reagents, their hardness and increased specific gravity, indicate a chemical union between the constituents. That in these alloys there are present a number of compounds, some of which are more stable than others, the latter being readily attacked by weak solvents. That these compounds are distributed with considerable uniformity throughout the mass of the alloy, segregation being the exception, not the rule, and that their freezing-points must be approximately the same, preventing the segregation of alloys of great density in any one portion of the alloys; that the more stable of these alloys are definite chemical compounds; that the less stable may be definite compounds or of the nature of cryohydrates or with one of the constituents present in the mixture in a state analogous to that of ice in a frozen salt solution in which water is in excess.

2. That, therefore, in these alloys the existence of definite compounds differing in their action toward solvents; their contraction as indicated by their specific gravity, hardness, etc., the fact that chemical union exists involving the breaking up of the

[1] Sterry Hunt, New Basis of Chemistry, p. 51 seq. and 100. Systematic Mineralogy, p. 86.

[2] Howe, Metallurgy of Steel, p. 254.

[3] *Bull. Soc. Chim.*, 11, 8, January, *1893*.

complex iron, molybdenum, tungsten, and chromium molecules and their union to form a new compound, *i. e.*, the passing of a heterogeneous system of molecules of like elements to a homogeneous system in the melted condition and again to a heterogeneous system in the resultant alloy; that these properties indicate a condition in these alloys analogous to an aqueous solution of a salt converted by cold to the solid state.

3. The high melting-point of the element in combination with the iron and its chemical affinity for iron is especially favorable to the separation of alloys from the cooling solution, and is the cause of the heterogeneity of these compounds. This separation of salts, *i. e.*, segregation, draws the analogy between these alloys and solutions closely.

XI. Composition of Alloys.

Alloys.	A.	B.	C.	D.	E.
Molybdenum	0.2979	0.1665	.....	.....	.....
Tungsten	.....	.....	0.4646	0.1696	.....
Chromium	.....	.....	.....	.....	0.0702
Iron	0.6626	0.7942	0.5251	0.7832	0.8799
Phosphorus	0.0031	0.0030	0.0004	0.0025	0.0029
Silicon	0.0074	0.0066	0.0014	0.0207	0.0337
Combined carbon	0.0017	0.0020	0.0075	0.0184	0.0041
Graphitic carbon	0.0273	0.0277		0.0056	0.0082

THE PROTEIDS OF THE KIDNEY BEAN.

(Phaseolus Vulgaris.)

By Thomas B. Osborne.

(*Continued from page 712.*)

Another trial was made by treating 400 grams of bean-meal, previously exhausted by benzine, with one per cent. sodium chloride solution, dialyzing the extract for twenty-four hours, and filtering off the precipitated phaseolin. The clear filtrate after standing over night, deposited a considerable quantity of proteid, but the solution with this deposit was returned to the dialyzer and left for two days longer, when it was filtered, the precipitate washed with water, alcohol, and ether, dried over sulphuric acid, and six grams of preparation 36 obtained.

PHASELIN, PREPARATION 36.

		Ash-free.
Carbon	50.44	51.41
Hydrogen	7.14	7.28
Nitrogen	14.31	14.59
Sulphur	0.46	0.47
Oxygen	....	26.25
Ash	1.94	....
		100.00

The filtrate from preparation 36 was then dialyzed into distilled water which was renewed every twenty-four hours for several days. After a week the solution was filtered and the precipitate washed with water, alcohol, and ether, and dried over sulphuric acid. It weighed 1.60 grams, 37.

PHASELIN, PREPARATION 37.

	I.	II.	Average.	Ash-free.
Carbon	51.38	51.22	51.30	52.19
Hydrogen	7.25	6.99	7.12	7.24
Nitrogen	14.52	....	14.52	14.79
Sulphur } Oxygen }	....	....	....	25.78
Ash	1.83	1.61	1.72	....
				100.00

One more preparation, 38, was made in the same manner as 37, and had the following composition:

PHASELIN, PREPARATION 38.

		Ash-free.
Carbon	50.20	51.27
Hydrogen	7.07	7.22
Nitrogen	14.02	14.32
Sulphur	0.50	0.51
Oxygen	....	26.68
Ash	2.06	....
		100.00

Further dialysis in distilled water, of the filtrate from preparation 37, gave no more precipitate. The solution was therefore saturated with ammonium sulphate, and the precipitate so produced filtered off and dissolved in distilled water. This solution which now had a volume of about 400 cc. was dialyzed for some

days, first in river water, and afterwards in distilled water, but only a trace of substance separated. This was filtered off, and the perfectly clear solution gave the following reactions:

Saturation with sodium chloride produced no precipitate until acetic acid was added. Acetic acid in the absence of salt gave no precipitate. Nitric acid gave a turbidity when added in considerable quantity, and the addition of some sodium chloride produced no further precipitation. Copper sulphate gave no precipitate. This solution when heated became turbid at 57° and particulate at 63°.

The entire solution was therefore heated to 70° in a water-bath which did not exceed this temperature, and after two hours, filtered from the separated coagulum. This was then washed with distilled water, alcohol, absolute alcohol, and ether, and dried over sulphuric acid. It weighed 0.48 gram. Before drying, this coagulum dissolved readily in two-tenths per cent. hydrochloric acid, and in dilute potash solution, and gave a violet reaction with copper sulphate and caustic potash. The filtrate from this coagulum gave a further small coagulum when heated at 70°, for some time longer. This was filtered off, and after treating it in the same way as the first coagulum, was added to it. The total amount of coagulum, preparation 39, amounted to 0.63 gram, and after drying at 110° was found to contain, ash-free, 15.23 per cent. of nitrogen.

The filtrate from 39 was then dialyzed into alcohol, and the solution thereby concentrated. On adding an equal volume of strong alcohol, the proteid was precipitated. This was filtered off, washed with absolute alcohol and ether, and dried over sulphuric acid. It then weighed 0.72 gram which shows that the proteids had been almost wholly precipitated by dialysis and coagulation.

This substance gave a nearly clear solution with distilled water, not made clearer by adding a few drops of sodium chloride solution. With caustic potash and copper sulphate, a pink color was developed which had a distinct violet tinge, and was by no means so red as that given by pure proteoses and peptones.

The aqueous solution heated to 85° gave a flocculent coagulum which apparently represented most of the substance. From

this, it would appear that true proteoses are present in extremely small amounts.

Dried at 110°, this preparation, 40, contained, ash-free, 13.60 per cent. of nitrogen. Being thrown down by strong alcohol, it could scarcely be pure, and the nitrogen determination is only of value, as indicating that the coagulum mainly consisted of proteid.

Of these preparations, 25, 27, and 32, are unquestionably mixtures of phaseolin and phaselin. Excluding these three and also 38 and 40, evidently impure, the remaining agree fairly well, as is shown by the following table:

SUMMARY OF ANALYSES OF PHASELIN FROM THE KIDNEY BEAN.

	26.	28.	29.	30.	31.	33.
Carbon	....	51.57	....	51.59	51.98	....
Hydrogen	....	6.92	....	6.71	6.82	....
Nitrogen	14.57	14.48	14.81	14.84	14.53	14.85
Sulphur } Oxygen }	....	27.03	....	26.87	26.68	....
	.....	100.00	.....	100.00	100.00	.....

	34.	35.	36.	37.	38.	Average.
Carbon	51.38	51.37	51.41	52.19	51.27	51.60
Hydrogen	6.91	7.10	7.28	7.24	7.22	7.02
Nitrogen	14.67	14.71	14.59	14.79	14.32	14.65
Sulphur } Oxygen }	.... 27.04	26.82	{ 0.47 / 26.25 }	25.78	{ 0.51 / 26.68 }	0.49 / 26.24
	100.00	100.00	100.00	100.00	100.00	100.00

It is probable that these analyses pretty closely represent the true composition of this proteid, the various preparations having been made under such diverse conditions as to exclude the possibility of their being mixtures of the phaselin with non-proteid substances.

Preparations 26 and 28 were precipitated by heat, 29 and 30 by acid. Preparations 31, 34 and 35 were thrown down by alcohol, extracted by water from the precipitate so produced, and separated from the solution—31 by acid, and 34 and 35 by dialysis in alcohol. Finally, 36, 37, and 38 were obtained by fractional dialysis in water.

There is some difficulty in deciding to what class of proteids phaselin should be assigned. It most nearly agrees with the

globulins, being precipitated by dialysis after nearly all the salts are removed, and thereby largely converted into an insoluble form. Complete precipitation is not accomplished, even by prolonged dialysis in distilled water, and it may be questioned whether the precipitation that occurs on dialysis in water, is not the result of transformation into "albuminate."

Nitric acid in sufficient quantity gives a precipitate which, on warming, does not dissolve in the manner characterizing proteoses. Saturation with sodium chloride, gives only a slight precipitate, but further addition of acetic acid, occasions an abundant precipitate. With copper sulphate and caustic potash a violet color is produced.

The coagulum produced by heat, dissolves in one-tenth per cent. hydrochloric acid when heated to 80°. The temperature at which coagulation commences, varies with the amount of salts present, a turbidity usually appearing between 40° and 50° in solutions which have been dialyzed until the greater part of the phaseolin had been separated. The ten per cent. sodium chloride extract of the bean-meal, became turbid at 52°–55°, flocks forming at 68°–70°. The aqueous extract of the meal, heated to 60° gave a turbidity but slightly increased by boiling. When ten per cent. of sodium chloride was added to the aqueous extract, turbidity occurred at 37° and flocks formed at 52°. The coagulation of this proteid by heat, proceeds very slowly and is completed only by very prolonged heating, for days even, at a temperature considerably higher than that at which flocks first appear.

Amount of Proteids in the Kidney Bean.

The quantities of these two proteids occurring in the kidney bean cannot be accurately determined, owing to the difficulties encountered in separating them. An approximate estimate is as follows:

1. A sample of freshly ground air-dry bean-meal yielded by combustion, 3.785 per cent. of nitrogen. Considering all the nitrogen to exist as proteids containing sixteen per cent. of this element, the proportion of proteids in the bean-meal would be $(3.785 \times 6.25 =)$ 23.65 per cent.

2. Twenty grams of bean-meal were treated repeatedly with

ten per cent. sodium chloride solution, until no more proteids could be extracted. The residue, after washing with water, alcohol, and ether, weighed, air-dry, 11.41 grams and contained 1.877 per cent. or 0.214 gram of nitrogen, equivalent to 1.338 grams of salt-insoluble proteid, which amounts to 6.69 per cent. of the meal. The salt-soluble proteids were accordingly (23.65 —6.69 = 16.96) seventeen per cent. of the meal.

3. In making preparations 4, 5, 6, and 7, pp. 638–9, the phaseolin obtained from the salt extract amounted to 14.77 per cent. This when weighed was not altogether pure or dry, but on the other hand, a part of this proteid existing in the salt extract, was not recovered, so that it may be fairly assumed that the meal contains about fifteen per cent. of salt-soluble phaseolin. This deducted from the seventeen per cent. of total salt-soluble proteids, leaves two per cent. for phaselin, reckoned water-free, other proteids being present in very minute quantity.

4. The preparations 36, 37, 39, and 40, pp. 758–60, were obtained from one and the same portion, 400 grams, of bean-meal, after phaseolin had been as completely removed as practicable. These preparations after drying over sulphuric acid, weighed respectively 6.00, 1.60, 0.63, and 0.72 grams, their total weight being 8.95 grams, equal to 2.24 per cent. of the meal. Their average nitrogen content was 14.54 per cent., very nearly that of phaselin. Making liberal allowance for impurities and incomplete drying, they represent about two per cent. of phaselin.

5. Twenty grams of bean-meal were extracted as completely as possible with two-tenths per cent. potash water. The washed and air-dry residue weighed 11.27 grams, and contained 0.91 per cent. or 0.1026 gram of nitrogen, equal to 0.611 gram of (water-free) proteid insoluble in alkali, or to 3.06 per cent. of the meal. The alkali-soluble proteid amounted therefore to (23.65 — 3.06 = 20.59) 20.6 per cent. of the meal.

6. On page 642 is recorded that the proteid insoluble in salt solution, but dissolved by two-tenths per cent. potash, 15, contained sixteen per cent. of nitrogen and accordingly had nearly the composition of phaseolin. It is, therefore, probable that the proteid undissolved by salt-solution, is phaseolin. On this assumption, the kidney bean examined, contains about 21.5

per cent. of phaseolin, and about two per cent. of phaselin.

7. The foregoing data are summarized as follows: The "white medium field bean" contains approximately:

Phaselin, salt-soluble	2	per cent.
Phaseolin, salt-soluble	15	"
Phaseolin, salt-insoluble, alkali-soluble	3.5	"
Phaseolin, insoluble in salt and in $\frac{2}{10}$ per cent. alkali	3	"
Total proteids	23.5	"

Schulze, Steiger and Maxwell have stated[1] that ten per cent. of the nitrogen of the seeds of the horse bean (*Vicia faba*) the vetch and the pea, exists in non-proteid form. Should such prove to be the case with the kidney bean, then its total proteids would be about twenty-one per cent. instead of 23.5 per cent.

Conclusion.

The kidney bean contains two globulins characterized by great solubility in very dilute saline solutions, and by yielding precipitates with acids which are soluble in sodium chloride solutions. One of these globulins, *phaseolin*, probably forms about twenty per cent. of the seed, and has the following composition, which is the average of analyses of twenty-four different preparations:

Phaseolin.

Carbon	52.58
Hydrogen	6.84
Nitrogen	16.47
Sulphur	0.56
Oxygen	23.55
	100.00

This is the proteid described by Ritthausen in 1884, to which he assigned very nearly the same composition as that above given.

The other proteid, *phaselin*, is much more soluble, remaining in solution after the phaseolin has separated. It is slowly coagulated by heat at temperatures varying with the amount of salts present and the rapidity of heating. It is precipitated by acids, on prolonged dialysis yields insoluble or albuminate modifications, and has more nearly the properties of a globulin

[1] *Versuchs Stationen*, 39, 306.

than of any other recognized class of proteids. It has an unusually low nitrogen and high oxygen content as shown by the subjoined average of the analyses of eleven different preparations.

PHASELIN.

Carbon	51.60
Hydrogen	7.02
Nitrogen	14.65
Sulphur	0.49
Oxygen	26.24
	100.00

In addition to these two globulins, the extracts were found to contain an extremely small amount of *proteose*.

MAY, 1893.

A SAFETY ATTACHMENT FOR RIDERS.

BY CHAS. E. PARKER, PH.C.

Received August 30, 1894.

SOME years since, an attachment for manipulating the weighing rider of balances was introduced by Verbeck and Peckholdt. The arrangement, devised by the writer, and here described, appears to have some advantages in simplicity, lightness, and adaptability.

It consists of a piece of sheet brass cut in the shape shown in *b*, Fig. 1, to which is soldered a bit of hair-spring from a watch, *a*; and of a light glass rod, *m*, Fig. 3, secured in a position parallel to the beam behind and slightly above it.

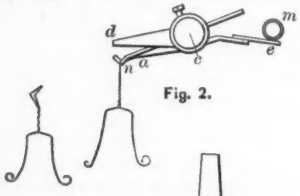

Fig. 2.

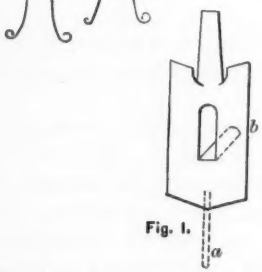

Fig. 1.

The piece of brass, *b*, is bent, as shown in Figs. 2 and 3, to form a sleeve upon the rod, *c*, together with a prong in apposition to the hook by which the rider is usually lifted, *n*, Fig. 2; and an extension, *e*, back under the rod, *m*, which thus limits the rotation of the sleeve and prong in one direction.

The operation is readily understood; the usual hook arrangement being converted into forceps

normally closed by the spring, *a*, thus securing the rider. When, by turning the rod, *c*, the rider is lowered, just before it rests upon the beam, contact between *m* and *e* checks the corresponding motion of the sleeve, thus opening the forceps; continuing

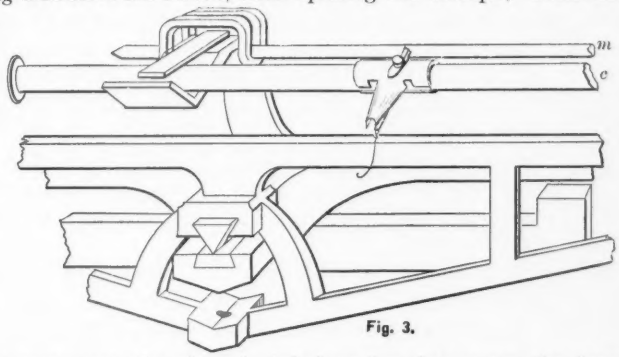

Fig. 3.

the movement, the rider is left hanging free upon the beam. Upon releasing the rod, *c*, the tension of the spring should be sufficient to close the forceps. When, however, it is often desirable to leave the rider upon the beam, by bending its loop, as shown in the side sketch, Fig. 2, this is easily effected.

Not the least advantage of this device is the readiness with which it can be extemporized.

ON THE ESTIMATION OF PHOSPHORIC ACID BY TITRATION OF THE YELLOW PRECIPITATE.

By B. W. Kilgore.

Received September 15, 1894.

METHODS based upon the principle of titrating the yellow precipitate with standard alkali have been described by a number of chemists, especially for the estimation of phosphorus in iron and steel and their ores, where it is present in very small quantities. Among them may be mentioned by abstract:

E. Thilo (abstract *J. Anal. Chem.*, **1**, part 2, 219, *1887*) in the estimation of P_2O_5 in Thomas Slag, precipitates at 70° C. with molybdic solution containing one part molybdic acid, three parts ammonium nitrate, and fifteen parts nitric acid, allows to stand five minutes, filters, washes with twenty per cent.

ammonium nitrate solution, and titrates with ammonium hydroxide and back with sulphuric acid.

C. E. Manby (*J. Anal. Appl. Chem.*, **6,** 82) precipitates near boiling, washes with three per cent. each nitric acid and potassium nitrate, dissolves in fifteen per cent. ammonium hydroxide, boils off the excess of ammonia, adds two cc. of nitric acid of 1.20 sp. gr., evaporates to dryness, heats sufficiently to expel nitric acid and ammonium nitrate, titrates with sodium hydroxide, and back with nitric acid.

J. O. Handy (*J. Anal. Appl. Chem.*, **6,** 204) precipitates at 85° C., shakes for five minutes, filters, washes five times with one per cent. nitric acid, five times with one per cent. potassium nitrate, and titrates.

M. Rothberg and W. A. Auchinvole (*J. Anal. Appl. Chem.*, **6,** 243) precipitates at 40° C., shakes for one minute, allows to stand in a warm place five more, filters, washes five times with one per cent. nitric acid, five times with three-tenths per cent. potassium nitrate, titrates with sodium hydroxide, and back with nitric acid.

Dr. Franz Hundeshagen (*Chem. News*, **60,** 168, 177, 188, 201, 215) in his analytical studies of ammonium phosphomolybdate, shows its composition under all conditions, when free of molybdic acid and other impurities, to be $12MoO_3 . PO_4 . 3NH_4$.

He washes the precipitate with five per cent. solution of ammonium nitrate, titrates with sodium hydroxide, and back with nitric acid. He found that it required twenty-three molecules of alkali to neutralize one molecule of ammonium phosphomolybdate.

And H. Pemberton, Jr., (*J. Am. Chem Soc.*, **15,** 382) has published the description of a method on this principle, which he applied to the determination of phosphoric acid in high-grade phosphates. He uses one-tenth gram substance for analysis, precipitates at boiling with aqueous ammonium molybdate, washes with water, titrates with potassium hydroxide, free from carbonates, and back with hydrochloric acid. In his first work, he found that it required 23.2 molecules alkali to neutralize one molecule ammonium phosphomolybdate, but in his later work he has obtained twenty-three molecules.

The writer has made quite a good many determinations of phosphoric acid in materials of varying percentages by this method, with fairly good results generally but with very wide variations at times, the tendency of the method being to give high results, although the yellow precipitate was washed liberally to remove free acid. It was believed that molybdic acid was the cause of the variations, as it was known that molybdic acid would deposit from other molybdic solutions very quickly at the temperature of precipitation used in the Pemberton method. To see if the aqueous molybdate was an exception to this rule, and also to see if the official molybdate of the Association of Official Agricultural Chemists would take the place of the aqueous solution, the official molybdate was used for precipitating at boiling temperature, the method as described by Pemberton being carried out otherwise, except that two-tenths gram of substance was used.

Results obtained in this way were less subject to variations than when the aqueous molybdate was employed, though high percentages would still often be obtained. Both molybdates were then tried side by side in the water-bath at temperatures of 70°, 65°, and 60° C., (this means practically 5° lower temperature in the beaker), allowing five minutes for precipitation, which was found in all cases to be complete. The results thus obtained were favorable to the lower temperature of 60° C. in bath and to the official molybdate, there being very few variations from the gravimetric method when precipitation was made at 60° C. and by official molybdate. A great many results were obtained in testing these and other points, but most of the early ones were not kept. In the following table are brought together some of the earlier results and all of the later ones by the volumetric method, either as carried out by Pemberton or myself or both, in the order in which they were obtained, and also results by the gravimetric method on the same samples for comparison. The gravimetric results were not duplicated. Among the earlier results by the volumetric method, there are quite a number of wide variations from the gravimetric results, but the later ones by the volumetric method as carried out by myself, nearly all show close agreement with gravimetric results.

DETERMINATION OF PHOSPHORIC ACID IN VARIOUS FERTILIZERS BY THE GRAVIMETRIC METHOD AND BY THE VOLUMETRIC METHOD AS CARRIED OUT BY PEMBERTON AND AS CARRIED OUT BY KILGORE.

No.	Official.	Pemberton.	Kilgore.	No.	Official.	Pemberton.	Kilgore.
1.....	10.40	....	10.34[1]	35.....	10.41	....	10.26[4]
2.....	9.48	....	9.40[1]	36.....	10.43	....	9.46[5]
2.....	....	....	10.52[1]	37.....	12.26	....	9.94[5]
3.....	2.44	....	2.53[1]	38.....	8.83	....	8.84[3]
4.....	2.85	....	2.78[1]	39.....	8.11	....	8.08[4]
5.....	3.90	....	3.83[1]	40.....	13.36	....	8.87[5]
5.....	....	....	3.80[1]	41.....	10.59	....	10.34[3]
6.....	0.08	....	0.30[1]	42.....	8.83	....	8.56[4]
7.....	2.17	2.18	....	43.....	9.17	....	9.26[3]
8.....	2.72	....	2.62[1]	44.....	9.12	....	9.17[2]
9.....	3.76	3.76	....	45.....	10.20	....	10.33[2]
10.....	15.58	....	15.48[1]	46.....	13.70	....	13.62[2]
10.....	....	....	15.40[1]	47.....	13.92	....	13.92[2]
11.....	14.09	....	13.96[2]	48.....	15.75	....	15.50[2]
12.....	13.61	....	13.36[2]	49.....	8.14	....	8.40[2]
12.....	....	....	13.60[2]	50.....	8.40	....	8.22[2]
13.....	12.98	....	13.06[1]	51.....	10.73	....	10.80[2]
14.....	9.79	10.60	9.60[2]	52.....	9.63	....	9.67[2]
14.....	....	....	9.70[2]	53.....	10.50	....	10.48[2]
15.....	9.95	10.25	9.90[2]	54.....	10.53	....	10.58[2]
15.....	....	10.20	9.83[2]	55.....	11.13	....	11.10[4]
16.....	1.25	....	1.14[2]	56.....	8.96	....	8.87[4]
17.....	2.64	....	2.56[2]	57.....	10.75	....	10.72[4]
18.....	1.68	....	1.58[2]	58.....	10.73	....	10.74[4]
19.....	4.06	4.05	....	59.....	11.63	....	11.53[4]
20.....	2.07	2.10	....	60.....	9.59	....	9.64[3]
21.....	1.37	1.31[2]	....	61.....	13.96	....	14.18[3]
22.....	2.14	2.19[2]	....	62.....	14.43	....	14.33[6]
23.....	1.30	....	1.23[2]	63.....	14.37	....	14.23[6]
24.....	3.93	....	3.93[2]	64.....	10.67	....	10.65[3]
25.....	10.90	10.87	....	65.....	9.49	....	9.55[3]
26.....	11.28	11.90[2]	....	66.....	10.61	....	10.77[3]
27.....	8.89	10.55	9.00[2]	67.....	10.93	....	11.11[3]
28.....	10.61	10.98	....	68.....	11.55	....	11.59[6]
29.....	9.93	10.14	....	69.....	12.60	....	12.45[6]
30.....	9.72	9.98	....	70.....	10.16	....	10.45[6]
31.....	10.59	10.96	....	71.....	14.80	....	14.77[6]
32.....	9.04	....	9.10[3]	72.....	9.95	....	10.20[2]
33.....	8.72	....	8.72[3]	73.....	9.93	....	10.22[2]
34.....	10.07	....	10.00[4]	74.....	9.63	....	9.80[2]

No.	Official.	Pemberton.	Kilgore.
75.....	10.52	....	10.49[7]
76.....	11.00	....	10.98[2]
77.....	10.68	....	10.71[7]
78.....	13.42	....	13.26[7]
79.....	12.63	....	12.60[7]
80.....	15.06	....	14.89[7]
81.....	14.79	....	14.84[7]
82.....	14.87	....	14.84[7]
83.....	12.22	....	12.17[7]
84.....	12.75	....	12.72[2]
85.....	12.46	....	12.34[7]
86.....	11.23	....	11.09[7]
87.....	9.03	....	9.12[7]
88.....	10.49	....	10.40[7]
89.....	15.43	....	15.30[7]
90.....	16.27	....	15.86[7]
91.....	15.98	....	15.61[7]
92.....	15.71	....	15.71[7]
93.....	11.83	....	11.63[7]
94.....	10.04	....	9.94[7]
95.....	13.28	....	13.25[7]
96.....	10.55	....	10.42[7]
97.....	10.41	....	10.40[7]
98.....	9.76	....	9.62[7]
99.....	11.26	....	11.25[2]
100.....	11.49	....	11.37[7]
101.....	15.83	....	15.73[7]
102.....	15.71	....	15.71[7]
103.....	15.25	....	15.20[7]
104.....	11.64	12.15	11.63[2]
105.....	15.89	16.20	15.71[2]
106.....	15.54	16.15	15.65[7]
107.....	15.20	16.17	15.25[2]
108.....	13.96	....	14.18[7]
109.....	13.60	....	13.67[7]
110.....	15.67	....	15.82[7]
111.....	11.80	....	11.85[7]
112.....	11.74	....	11.75[7]
113[8]	19.93	20.35	19.85[7]
	19.83	20.15	19.95[7]
	19.91	20.15	19.90[7]
	19.85	20.10	19.80[7]
114	17.17	17.20	17.15[7]
	17.12	17.40	17.10[7]
115.....	2.42	....	2.47[7]

[1] Precipitated at boiling.

[2] Precipitated in bath at 70° C.

[3] Precipitated in bath at 65° C.

[4] Precipitated in bath at 65° C. with the addition of five cc. HNO_3 to fifty cc. molybdic solution (official).

[5] Same as 4 with ten cc. HNO_3.

[6] Same as 4 with three cc. HNO_3.

[7] Precipitated in bath at 60° C.

[8] C. P. $Na_2HPO_4 + 12H_2O = 19.826$ per cent. P_2O_5.

There are two main differences in the volumetric method as carried out by Pemberton and as carried out by myself. First, the temperature of precipitation in the former is at boiling; in the latter 60° in bath or 55° C. in beaker. At the former temperature molybdic acid deposits very quickly, especially if any considerable excess of the precipitant is present. If we know how much phosphoric acid our samples contain and add just enough molybdate to do the work, or are willing to add little by little of the precipitating reagent till the proper amount has been added, this objection is largely overcome, but the former we do not know and the latter is tedious and time-consuming,

especially when large numbers of analyses are being carried on at once. At 55° C., the official molybdate does not deposit, at worst, for fifteen minutes or more; precipitation is always complete in four or five minutes from the time the molybdate is added, and precipitation and filtration can be finished in almost, if not in, as short a time by this method of procedure as by the regular Pemberton method, with the advantages of less danger of molybdic acid depositing, and of being able to handle a larger number of determinations at once.

The second difference is in the two molybdic solutions. The official molybdic solution contains practically sixty grams MoO_3 to the liter, and the Pemberton solution, sixty-six grams to the liter, so there is no very great difference in their precipitating powers. In the official molybdate the proportion of free nitric acid to molybdic acid is always the same, being equivalent to nearly fifteen cc. 1.42 sp. gr. acid to fifty cc. molybdic solution; while in Pemberton's molybdate the quantity is just five cc. 1.42 sp. gr. nitric acid, no matter whether twenty-five cc. or fifty cc. of the aqueous molybdate is added. It will be readily understood that should any considerable excess of this aqueous molybdate be added (and such a thing is liable to be done), and there being only five cc. nitric acid to hold it in solution, precipitation of molybdic acid would be sure and quick. To see which of the two molybdates was most liable to deposit molybdic acid under the same conditions, the conditions being as nearly as possible those of precipitation without the phosphate, the following experiments were made: Fifty cc. official molybdate, containing three grams MoO_3 and fifteen cc. nitric acid were diluted with fifty cc. water; and to forty-five cc. of Pemberton's molybdate, containing 2.97 grams MoO_3, were added, ten cc. saturated solution of ammonium nitrate, five cc. nitric acid, and forty cc. water. Both mixtures, being of the same volume and containing the same amount of molybdic acid, were placed in a water-bath at 60° C. The mixture of official molybdate showed no deposit for over twenty minutes, but a considerable one in one hour; the other mixture deposited seemingly the whole content of molybdic acid in less than four minutes and in fact this mixture could not be made to stand in the cold over three

or four minutes without throwing down great volumes of molybdic acid; but forty-five cc. and fifty cc. of the two molybdates are too much to precipitate the phosphoric acid from two-tenths gram substance, but not much in excess of safe quantities for most materials where four-tenths gram substance is used. With two-tenths gram substance, one-half the above quantities are about the right amounts to use. Experiments with them similar to the foregoing, were made as follows: Twenty-five cc. of official molybdate, containing one and five-tenths grams MoO_3 and seven and five-tenths cc. nitric acid were diluted with five cc. water; and to 22.5 cc. of Pemberton's molybdate, containing 1.48 grams MoO_3, were added five cc. nitric acid, ten cc. ammonium nitrate solution, and 12.5 cc. water. Both mixtures, being of the same volume and containing the same amount of molybdic acid, were allowed to stand as before. The mixture of official molybdate deposited about as in the first experiment; the Pemberton one remained clear for ten or fifteen minutes, when it commenced to get cloudy and in twenty minutes it was milky and a heavy deposit had formed. Seventeen cc. of the official molybdate and fifteen cc. of the Pemberton one contain the same amounts of MoO_3 and when these quantities are used for precipitating equal amounts of nitric acid, five cc., are present in each case. When these amounts were diluted to fifty cc. and allowed to stand at 60° C. the deposits were the same as in the official molybdate in the two preceding experiments, which argues that the official molybdate contains about the right amount of nitric acid to prevent deposit of molybdic acid, and at the same time allow quick precipitation of phosphoric acid.

The aqueous molybdate as used in the Pemberton method works well when added in just the proper quantities, but there is not enough free nitric acid present to allow of much marginal excess. The official molybdate seems to contain a very large amount of free nitric acid. To test the effect of still larger quantities of free acid, the results in the table, as designated by the foot-notes, show that ten cc. additional nitric acid of 1.42 sp. gr. to fifty cc. molybdate hindered precipitation greatly; five cc. prevented its being complete in five minutes; while three cc. additional did not seem to interfere. The more free nitric acid

present, not to interfere with precipitation, the less liability there is of molybdic acid depositing. Just here I would add that the deposit from the official molybdic solution, at least, is not molybdic acid alone but a mixture of molybdic acid and ammonium molybdate. I found one deposit to contain 1.21 per cent. NH_3.

The volumetric method as it has given me best results is as follows: Make solution as per the official nitric and hydrochloric acid method for total phosphoric acid, redissolve two grams substance in thirty cc. strong nitric acid and five to ten cc. hydrochloric acid, measure out twenty cc. for total or forty cc. for insoluble, corresponding to two-tenths and four-tenths gram substance respectively, into a four-ounce beaker, add ammonia till precipitate just begins to form, and dilute to seventy-five cc. If much of the nitric acid was driven off in making the solution add ten to fifteen grams ammonium nitrate, otherwise this is not necessary. Digest in water-bath at 60° C., and after filtering the molybdate[1] used in the official method, precipitate in the usual way, allow to stand four or five minutes from the time the molybdate is added, filter as quickly as possible upon either a filter made by putting a platinum cone or disk, well filled with holes, into a three-inch funnel and covering with coarse asbestos, or upon the Hirsch funnel, or preferably upon a porcelain disk (the disk to be covered with filter paper) with rubber rim in three-inch glass funnel, using the pump in all cases. Wash the precipitate three to five times by decantation, using fifty to seventy-five cc. water each time and agitating thoroughly, then onto the filter and till no longer acid, titrate with potassium hydroxide and back with nitric acid.

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THE QUALITY OF WATER SUPPLIES.[2]

BY WM. P. MASON.

A PAPER of some length, bearing the title "The Quality of Water Supplies," has just been presented before the American Society of Civil Engineers, at their Niagara meeting, which contains considerable matter provoking comment. The

[1] This solution is made by dissolving 100 grams molybdic acid in 417 cc. 0.96 sp. gr. ammonia, and pouring this into 1,250 cc. 1.20 sp. gr. nitric acid.

[2] Read at the Brooklyn meeting August 16, 1894.

author appears to be a believer in the power of water to spread disease; but some of the statements and quotations advanced by him would certainly go far to unsettle the public mind and cause lack of faith in the teachings of some able masters.

He says: "While water is held to be a carrier of disease germs, the writer is not aware that any investigator has ever claimed to have seen these germs in water, even under the highest powers of the microscope; and the evidence that water is such a carrier of pathogenic bacteria is obtained by inoculation from water samples, of nutrient media in test-tubes or on culture plates. The typhoid bacillus in water has never been seen with the microscope without previous cultivation of the germ in nutrient media. Nor has it ever been demonstrated, so far as the writer is aware, that the presence of bacilli in water can be proven, excepting by delicate and difficult bacteriological processes."

That single individuals of the Eberth bacillus should escape direct detection is hardly to be considered surprising, in view of the enormous volume of water in which they are suspended. However difficult the processes of modern bacteriology may be for a tyro, it is hardly just to consider them unreliable in the hands of Koch, Pasteur, or Eberth; and if any one of these men, or of many other who might be named, should state that he had secured pure cultures of a specific germ, under circumstances which excluded the possibility of extraneous contamination, we should be exceedingly liable to believe him.

Again: "It is well understood that the infective element of typhoid fever can be present in water, and the chemical test be powerless to disclose it."

True enough! but it does not complete the story. The contaminated waters were pronounced pure. It must be remembered that the polluting material, as weighed, being very largely water, the pollution appeared greater than it really was. During an investigation following a serious outbreak of typhoid fever in the Tees Valley, England, the medical officer of the Local Government Board, London, caused preparation to be made of samples of pure water, to which small quantities (fifty and twenty-five parts per million) of typhoid dejecta had been added,

and these samples were then submitted to prominent water analysts for examination. No results upon which an adverse report could be based were obtained. Fifty parts per million of the typhoid dejecta corresponded to only four parts per million of total dry residue. As a natural result of these experiments, the purely chemical methods of water examination received very severe criticism, and the advocates of the exclusively bacteriological processes were correspondingly elated, for here were known instances of fatal contamination, which the chemists had failed to diagnose. Let this, however, be said in defense: In cases as they occur in practice, a serious addition of typhoid dejecta has much that is associated with it, of a comparatively inoffensive character, but which reacts with the chemical reagents, and tells the tale of sewage contamination, although the analyst can not venture to state the exact nature of the source whence the pollution is derived.

Not long since, the writer claimed that the river water furnishing a large Eastern city was contaminated with up-stream sewage, the opinion having been based not alone upon an analysis of the water at the intake, for the river was large and the consequent dilution great, but upon the difference between that analysis and one of the water taken from above the sewage inflow. The difference was small, but it was noticeable, and there was no other sufficient explanation of its existence than the one given. Later on, typhoid fever broke out in the upper valley, and epidemics developed not only in the city in question, but in all the neighboring towns using the river water for supply. Closely related cities and towns, which received their water from other sources, were not affected. Space does not permit of giving details, showing how clearly the case stood against the river water, but it is interesting to note that typhoid germs were most carefully sought for and were not found. That they were nevertheless present, there can be but little doubt.

Chemical analysis in this instance did certainly not detect the presence of typhoid, but what it did do, was to warn the people, months before the typhoid appeared, that they were drinking diluted sewage, and that they must beware of the time when that sewage came from pathogenic sources.

The paper in question goes on to say:

"The popular impression that the Koch or Finkler and Prior comma bacillus is the cause of cholera is fallacious, or, at least, not proven. The same remark applies to the typhoid bacillus of Eberth. The proof is still wanting that this will cause typhoid." This last is a quotation from Sternberg's Manual of Bacteriology, but it is very misleading because it is incomplete.

What Sternberg really says is this: "Recent researches support the view that the bacillus described by Eberth, in 1880, bears an etiological relation to typhoid fever; and pathologists are disposed to accept this bacillus as the veritable germ of typhoid fever, notwithstanding the fact that the final proof that such is the case is still wanting. This final proof would consist in the production of man, or in one of the lower animals, of the specific morbid phenomena which characterize the disease in question, by the introduction of pure cultures of the bacillus into the body of a hearty individual. Evidently it is impracticable to make the test upon man, and thus far we have no satisfactory evidence that any one of the lower animals is subject to the disease, as it manifests itself in man." Now that is a very different statement, and conveys a meaning greatly unlike the one suggested by the partial quotation referred to.

The paper says: Absolutely healthy persons have been known to reject the Eberth bacillus in their excrement, showing such, probably, to be in the intestines at all times." This is an error. To use the words of Sternberg, from whom the paper so often quotes: "No competent bacteriologist, so far as I know, has claimed to find the Eberth bacillus in the feces of healthy individuals."

As to the doubt thrown upon the correctness of the view that Koch's comma bacillus is the cause of cholera, the work of Sternberg will hardly endorse it. In this connection Sternberg says: "The etiological relation of this spirillum to Asiatic cholera is now generally admitted by bacteriologists," and also, "the most satisfactory evidence that this spirillum is able to produce cholera in man, is afforded by an accidental infection which occurred in Berlin in the case of a young man who was one of the attendants at the Imperial Board of Health when

cholera cultures were being made for the instruction of students."

As to the statement in the paper that "fatal cases of typhoid have been attended with none of the Eberth bacillus in the feces, or in the intestines, the seat of the disease," it is to be noted that Gaffky's investigations show it to be by no means a serious objection. He considers the technical difficulties surrounding a hunt for the bacillus in some few instances so considerable as to readily account for a small percentage of negative results, and he cites instances where he found the "germ" after an amount of patient search extending far beyond the point where the average observer would have ceased work and placed a negative report upon record.

Finally, the paper has much to say upon the imperfections of modern filters and the danger of using water therefrom. It goes without saying that pure water is better than purified water, but then the former is often unattainable, and we have to do with the latter or go without.

The paper lays especial stress upon the fact that even when the filtration is so successfully accomplished as to leave in the filtrate only one or two bacteria per cubic centimeter, yet "a person may imbibe from 250 to 500 bacteria in drinking a single glass of water, some of which may be pathogenic and produce typhoid fever, or some less dangerous disease." Such a degree of excellence in filtration as the obtaining of a filtrate with only one or two bacteria per cubic centimeter is indeed rarely attained, yet the public have a right to look with confidence upon a plant which does not pretend to accomplish half that amount of purification.

Consider for a moment what the Altona filters did for that city during the Hamburg cholera epidemic of 1892. The Altona water was taken from the Elbe river at a point below the outfalls of sewers carrying the cholera-infected sewage of 800,000 people. Yet Altona had but very little cholera (except imported cases), while Hamburg was scourged by it. The cities are practically one, a stranger being unable to tell the dividing line.

Take the numbers showing the efficiency of the Altona filters during one month of 1892:

The bacteria in the raw Elbe water per cubic centimeter varied from 9,370 to 44,140, with an average of 28,667. The average number in the filtered water was ninety. This meant a removal of 99.69 per cent. of germs of all kinds, 0.31 per cent. still remaining. The filtrate was by no means sterilized, but the city was protected from a cholera epidemic under circumstances trying in the extreme. As to the efficiency of sand filtration for water purification, the following figures are given for results found at the Lawrence experiment station, the filters having been operated with water containing known quantities of bacteria:

Rate in gallons per acre daily, 1,500,000; kind of bacteria added, B. typhi. abdom.; per cent. removed, 99.93; rate in gallons per acre daily, 3,000,000; kind of bacteria added, B. prodigiosus; per cent. removed, 99.95.

This reduction of the number of germs in a given volume of water is possibly equivalent to a dilution of the unfiltered water with a very large volume of a pure supply; and in this connection the writer of the paper says: "Dilution may reduce the chances of any single individual imbibing a fatal germ, but the germ itself will be just as dangerous when it is imbibed."

This is, doubtless, true if the individual be especially susceptible, for it has been experimentally shown that a single germ may produce fatal results when injected into an animal very prone to the special disease, but it has been also shown that when the animal is not very susceptible, the "dose" of bacteria has to be enormously increased to produce any result. We incline to believe that some similar reason may account for the apparent immunity of that fraction of a community, which has been equally exposed but which escapes contagion.

What the paper says regarding the unsatisfactory results observed where household filters are in use, is, unfortunately, very true, but the fault is more commonly with the attendant than with the filter. The common belief is that a filter, once established, is good for all time, and I could tell tales of what I have seen, in otherwise well-organized establishments, that would stagger belief. I do not approve of general household filtration, as I believe purification can be better and more cheaply done on

the large scale by the municipal authorities, but I can not think that the Pasteur filter should be swept aside like the worthless contrivance the paper calls it. My experience is that, with proper care, it is efficient. Extended tests were made with it for the Connecticut Board of Health in 1892, which show that it may be depended upon, if the procelain cylinder be cleaned and sterilized once a week.

Freundenreich has obtained similar results, and has also shown that the length of time during which the filter is efficient depends upon the temperature.

RENSSELAER POLYTECHNIC INSTITUTE,
August, 1894.

THE PROTEIDS OF COTTONSEED.[1]

BY THOMAS B. OSBORNE AND CLARK G. VOORHEES.

THE only reference to the proteids of cottonseed which we can find was made by Ritthausen in 1881 (*J. prakt. Chem.*, **23**, 485), who stated that he had been unable to obtain crystals of proteid matter from this seed and also that he would soon publish his complete investigations of the proteid bodies of this as well as of several other seeds which he named. Papers on the proteids of the other seeds mentioned by him were subsequently published, but we have not found anything relating to those of cottonseed. Since so long a time has elapsed, we feel warranted in assuming that Ritthausen has abandoned his intention of reporting the results of his investigation. The importance which cottonseed-meal has assumed as a cattle-food of late years, makes it desirable to understand its chemical composition, especially as regards the nitrogen compounds which it contains so abundantly. Our results are not as satisfactory as we hoped for when we undertook this work but we have decided to publish them as they stand and shall endeavor to make them more complete in the future. The difficulties encountered are due to the presence of substances which render filtration of the extracts extremely slow and to the large amount of coloring matters taken up from the seed together with the proteids, which could be separated only with difficulty and large loss of substance. The material used in our investigation consisted partly of seed

[1] First printed in the Report for 1893 of the Connecticut Agricultural Experiment Station.

from which the cotton had been removed, but which otherwise was in the condition in which it was harvested. We separated the kernels from these seeds by chopping them in a wooden bowl and sifting out the larger fragments of husk. We thus succeeded in obtaining meal nearly free from hulls. This meal was bruised in a mortar and freed from most of the oil by extraction with benzine and from benzine by drying in the air at the temperature of the room. Samples of commercial cottonseed-meal from which the oil had been expressed by the usual process were also used and gave the same result when extracted, and therefore in the following account of our experiments, no special mention is made of the origin of the meal employed.

a. Extraction with Water.—100 grams of cottonseed-meal were extracted with three liters of distilled water and the filtered extract saturated with ammonium sulphate. The small precipitate so produced was filtered off, dissolved in water, the solution filtered clear and placed in a dialyzer. After remaining a week in running water, no precipitation occurred, showing the absence of any notable quantity of globulin soluble in the dilute saline solution produced by the salts of the seed with the water used in the extraction. The dialyzed solution gave no immediate coagulum on boiling, proving the absence of albumens. The solution was then evaporated over a lamp and, after boiling some time, a light, bulky coagulum gradually separated. When the solution became quite concentrated, the coagulum was filtered off, washed with water, alcohol, and ether, dried over sulphuric acid and found to weigh 0.25 gram. The filtrate from this coagulum was evaporated to small volume on a water-bath and precipitated by pouring into absolute alcohol. The precipitated proteid was then washed with absolute alcohol and ether and weighed, when dry, 0.40 gram. Accordingly, 0.65 per cent. of the oil-free meal, consisted of water-soluble proteose-like matter. The amount of this substance was so small, and the difficulty of preparing it in a state of purity so considerable, that it was not further examined. Other experiments, both with water and saline solution, fully confirmed the results here described and left no doubt that the amount of water-soluble proteid is very small.

b. Extraction with Sodium Chloride Solution.—When treated with ten to twenty per cent. sodium chloride solution, the cottonseed-meal yields a slightly acid extract of a yellowish-pink color which is viscid, and difficult to filter. When heated slowly, this extract becomes turbid at 44°, flocks, in small amount, separating at 64°. Filtered after heating to 70°, the solution becomes turbid when heated again to 70° and flocks in larger amount separate at 93°.

Saturation with sodium chloride gives a slight precipitate. Dilution of the extract with water yields an abundant precipitate which is redissolved on warming and again separates in the form of spheroids when cooled.

Fifty grams of oil-free meal were extracted with ten per cent. sodium chloride solution, and the meal washed with the same solution as long as any proteid could be extracted. The extract and washings were saturated with ammonium sulphate, the precipitate produced filtered off, dissolved in dilute sodium chloride brine, filtered, and dialyzed four days. The solution was then removed from the dialyzer and the precipitated globulin filtered off, washed with water, alcohol, and ether, and dried over sulphuric acid. There was thus obtained seven grams or fourteen per cent. of light yellowish proteid which, when dried at 110°, had the composition given below, preparation 1.

A second preparation was made by treating 100 grams of meal with three liters of twenty per cent. sodium chloride solution for forty-eight hours and, after filtering, saturating the extract with ammonium sulphate. The meal-residue was again treated with twenty per cent. sodium chloride brine and after filtering the extract, it was saturated with ammonium sulphate and added to the first.

The ammonium sulphate precipitate was filtered off and dissolved in ten per cent. sodium chloride solution, yielding a deep brown liquid. This was filtered clear and dialyzed till free from chlorides when the precipitate was filtered off and treated in the usual way. There resulted 15.83 grams of globulin of a slightly yellowish color which had the composition stated below, preparation 2.

A third preparation was obtained by extracting 100 grams of

meal with water and then treating the residue with twenty per cent. sodium chloride solution.

The salt-extract was filtered, saturated with ammonium sulphate and otherwise treated in the manner already described in making preparations 1 and 2. Only 8.39 grams of globulin were recovered, indicating a conversion into the insoluble modification through contact with water.

The composition of this preparation 3, is shown by the following figures.

COTTONSEED GLOBULIN.

	1				2				3	
	I.	II.	Av.	Ash-free.	I.	II.	Av.	Ash-free.		Ash-free.
Carbon	51.85	....	51.85	51.91	51.75	....	51.75	51.86	51.66	51.77
Hydrogen	6.78	....	6.78	6.79	6.87	....	6.87	6.88	6.73	6.74
Nitrogen	18.02	18.12	18.07	18.09	17.90	18.15	18.03	18.07	17.93	17.97
Sulphur	0.68	....	0.68	0.68	0.67	....	0.67	0.67	0.71	0.71
Oxygen	....	....	....	22.53	....	....	....	22.52	....	22.81
Ash	0.11	....	0.11	....	0.21	....	0.21	....	0.22	....
				100.00				100.00		100.00

The properties and composition of this substance are so similar to those of the vegetable vitellin found in the seeds of flax, hemp, wheat, and other seeds, it seemed probable that the three preparations just described were not entirely pure and that if freed from all foreign matters they would agree more closely with the globulin of the seeds just named. Three preparations were accordingly made, substantially in the manner already described and, after drying over sulphuric acid, they were redissolved in ten per cent. sodium chloride brine and the resulting clear solutions were dialyzed. The globulin thus reprecipitated, was filtered off, thoroughly washed with water, alcohol, and ether and when dried at 110° analyzed with the following results:

COTTONSEED GLOBULIN. EDESTIN.

	4		5		6			
		Ash-free.		Ash-free.	I.	II.	Av.	Ash-free.
Carbon	51.59	51.75	51.56	51.93	51.68	51.58	51.63	52.05
Hydrogen	6.68	6.70	6.92	6.97	7.11	6.92	6.97	7.02
Nitrogen	18.72	18.78	18.40	18.52	18.66	18.40	18.53	18.68
Sulphur	0.75	0.75	0.50	0.51	0.66	....	0.66	0.66
Oxygen	....	22.02	....	22.07	....	....	....	21.59
Ash	0.33	....	0.74	....	0.82	....	0.82	....
		100.00		100.00				100.00

We next attempted to detect the presence of other globulins in the sodium chloride extract. One kilogram of cottonseed-meal was extracted with ten per cent. sodium chloride solution and as the extract after straining through cloth was quite concentrated and could not be filtered, it was shaken with ether so as to remove oil and other substances soluble in that liquid. On standing, a part of the aqueous solution separated, leaving a supernatant layer consisting of an emulsion which long standing failed to resolve. Addition of alcohol, instead of breaking up the emulsion, transformed it into a jelly-like mass of considerable solidity. The unemulsified part of the extract, after standing some time, was decanted and dialyzed free from chlorides. The dialyzed solution was allowed to stand until the globulin had deposited when the supernatant liquid was decanted. The separated globulin was treated with ten per cent. sodium chloride brine and the solution filtered very nearly clear. This solution was then dialyzed for eighteen hours, during which time a large precipitate formed which was filtered off, washed with water, alcohol, and ether, and, when dried over sulphuric acid, weighed 23.63 grams, preparation 7. The filtrate was found to be practically free from proteids. The solution decanted from the first precipitation of the globulin contained a large amount of very finely divided substance that would not settle. A little sodium chloride was therefore added which dissolved the suspended globulin. The solution was next saturated with ammonium sulphate and the large precipitate filtered off, dissolved in water, the solution filtered perfectly clear, and dialyzed for several days. It was then removed from the dialyzer and allowed to stand until the suspended globulin had mostly settled out. The milky solution was then decanted from the sediment and the latter washed with water, alcohol, and ether. After drying over sulphuric acid it weighed 8.58 grams. Preparation 8. The solution decanted from 8, after repeated filtration was obtained clear and was again dialyzed. After several days a very small precipitate formed which, when subjected to the usual treatment, weighed but 0.82 gram. This was much colored and evidently impure. The solution filtered from this precipitate was saturated with ammonium sulphate and yielded

only a very small precipitate which appeared to consist mostly of proteose. The emulsion obtained by shaking the original extract with ether, after standing some days, gave no evidence of re-solution. The jelly-like mass was therefore broken up and thrown on a filter. A clear quick-running filtrate was obtained which was dialyzed for five days and deposited a globulin, that, after the usual treatment, weighed 8.43 grams. Preparation 9. All these preparations were analyzed with the following results:

COTTONSEED GLOBULIN. EDESTIN.

	7				8		9	
	I.	II.	Av.	Ash-free.		Ash-free.		Ash-free.
Carbon	51.59	51.45	51.52	51.75	51.38	51.44	51.10	51.33
Hydrogen	7.04	6.70	6.87	6.90	6.70	6.70	6.88	6.91
Nitrogen	18.76	18.71	18.74	18.82	18.49	18.51	18.47	18.55
Sulphur	0.61	....	0.61	0.61	....	23.05	0.60	0.60
Oxygen	....	....	....	21.92	....		....	22.61
Ash	0.46	....	0.46	....	0.12	....	0.46	....
				100.00		100.00		100.00

The above analyses show that the first three preparations were not quite pure and the extract, last made, affords satisfactory evidence that no other salt-soluble globulin exists in the cotton-seed in noteworthy amount. In the following table, the analyses of the purer preparations may be compared together.

SUMMARY OF ANALYSES OF COTTONSEED GLOBULIN. EDESTIN.

	4	5	6	7	8	9	Average.
Carbon	51.75	51.93	52.05	51.75	51.44	51.33	51.71
Hydrogen	6.70	6.97	7.02	6.90	6.70	6.91	6.86
Nitrogen	18.78	18.52	18.68	18.82	18.51	18.55	18.64
Sulphur	0.75	0.50	0.66	0.61	23.05	0.60	0.62
Oxygen	22.02	22.08	21.59	21.92		22.61	22.17
	100.00	100.00	100.00	100.00	100.00	100.00	100.00

The table subjoined shows that this substance agrees in composition with the vitellin which exists in the seeds of wheat, maize, hemp, castor-bean, squash, and flax. As the properties of the preparations obtained from all these sources are substantially alike, there can be little doubt that one and the same proteid exists in them all. For this body we adopt the name *Edestin*, from the Greek ἐδεστὸς, signifying edible, in view of its occurrence in so many important food-stuffs.

COMPOSITION OF EDESTIN FROM VARIOUS SEEDS.

	Wheat kernel.	Maize kernel.	Hemp-seed.	Castor-bean.	Squash seed.	Flax-seed.	Cotton-seed.
Carbon.....	51.03	51.71	51.28	51.31	51.66	51.48	51.71
Hydrogen..	6.85	6.85	6.84	6.97	6.89	6.94	6.86
Nitrogen...	18.39	18.12	18.84	18.75	18.51	18.60	18.64
Sulphur ...	0.69	0.86	0.87	0.76	0.88	0.81	0.62
Oxygen	23.04	22.46	22.17	22.21	22.06	22.17	22.17
	100.00	100.00	100.00	100.00	100.00	100.00	100.00

The considerable differences in carbon and nitrogen in the above analyses amounting, in the extreme cases, to 0.7 per cent. are, in general, not greater than the discrepancies between analyses of preparations from the same seed. In the seeds of wheat and maize, other water and salt-soluble proteids occur in considerable quantities and it is probable that the crystallized preparations obtained from hemp, castor-bean, squash, and flax more truly represent the composition of edestin than the amorphous or spheroidal substance yielded by the cereal seeds.

The slight differences in the deportment of solutions of these preparations of edestin may be reasonably attributed to admixtures of traces of other proteids.[1]

c. Extraction with Potash Water.—After extraction with water and sodium chloride solution a considerable amount of proteid was always found in the residual-meal which could be partly removed by two-tenths per cent. potash solution. All attempts to obtain the proteid thus extracted in a pure state, have hitherto entirely failed. Much coloring matter passes into the alkaline solutions, and when the proteid is precipitated, goes down with it and can not be removed by any process we have hitherto applied.

When freshly prepared, the alkaline extracts, as well as the meal moistened with the alkali, are of a bright reddish-yellow color, but on exposure to the air they rapidly darken and finally become greenish-black. So much gummy matter is also extracted by alkaline solutions that it is almost impossible to filter them clear. As a result no preparations were obtained, the analysis of which could shed any light on the composition of the proteid which they represented. The residue of meal after treatment with potash still contains a notable quantity of nitrogen.

[1] See paper on Crystallized Vegetable Proteids, by T. B. Osborne, *Am. Chem. J.*, 1 688.

d. Amounts of the Different Forms of Proteids in Cottonseed.—As already shown, the proteid matter of cottonseed soluble in water, consists almost wholly of proteose. Making full allowance for incomplete extraction and loss, this does not exceed 0.75 per cent. of the oil-free meal. The highest yield of globulin recovered in the preceding extractions was 15.83 per cent. of the oil-free meal, and contained 42.3 per cent. of the total nitrogen. After repeated extraction with potash water, the residue contained, in the case where extraction was most complete, 11.4 per cent. of the total nitrogen, showing that 88.6 per cent. of the total nitrogen had been dissolved. The difference between the percentage of nitrogen removed by sodium chloride solutions and that extracted by weak potash, represents the proteid dissolved by potash water which is not soluble in saline solutions, and which corresponds to 46.3 per cent. of the total nitrogen, assuming all this nitrogen to be present in proteid form.

These data may be tabulated as follows:

	Per cent. of Air-dry and oil-free meal.	Total nitrogen.
Proteose	0.75	2.0
Salt-soluble proteid. Edestin	15.83	42.3
Alkali-soluble and salt-insoluble proteid	....	44.3
Proteid insoluble both in salt and alkali	....	11.4
		100.0

ON THE ANALYSIS OF AMERICAN REFINED COPPER.[1]

By Harry F. Keller.

IT is generally conceded that the presence even of minute quantities of other elements in metallic copper has a marked influence upon its physical properties, and especially upon its electric conductivity.

The copper produced in the Lake Superior region is relatively free from injurious admixtures, and is, therefore, generally preferred when a high conductivity is desired. "Lake" copper is always quoted a trifle higher than the metal from other localities.

Of late years the production of copper from impure sulphide ores has grown enormously, and, at the same time, the quality of the product has steadily improved. It has, indeed, become

[1] First printed in the Journal of the Franklin Institute, July, 1894.

possible through the introduction of the Manhés converter and the electrolytic process of refining, to obtain from matte a metal nearly, if not quite, as pure as the native copper of Lake Superior. Unfortunately, it appears that the very slight traces of the impurities retained in it affect the conductivity to a greater extent than is the case in the best lake copper. Silver and iron are the chief impurities of the latter, while electrolytic copper not infrequently contains small quantities of bismuth, antimony, arsenic, selenium, and tellurium.

That the exact manner in which these elements affect the physical properties of copper is not better understood, is, undoubtedly, owing to the lack of rapid, and at the same time accurate, methods of ascertaining their relative amounts. It is astonishing to note that the works on quantitative analysis, published in the English language, entirely neglect copper analysis. To my knowledge the important contributions to this subject by Hampe, Fresenius and other German chemists have not been translated.

For several years past I have given considerable attention to this subject. My analyses include the metal from the Lake mines, as well as copper obtained from Western mattes.

To the former, I found Hampe's original method[1] of analysis well adapted. This consists essentially in precipitating, by electrolysis, the greater part of the copper, and separating the metallic impurities in the usual manner from the remaining solution. The non-metallic elements such as oxygen and sulphur, are determined in separate portions of the sample.

For obvious reasons it is not desirable to employ this method in analyzing electrolytically refined copper. Accurate results can be obtained by following the plan proposed by Fresenius,[2] but the separation of large quantities of copper by means of hydrogen sulphide, and the difficulty of accurately weighing bulky solutions, render this method very objectionable. A far more convenient process is the one recently published by Professor Hampe.[3] It is also more rapid than either of the two methods mentioned, and, with some modifications, it is especially

[1] *Ztschr. f. Berg. Hütten u. Salinenwesen*, **21**, 218, and **22**, 93.
[2] *Ztschr. anal. chem.*, **21**, 229.
[3] *Chem. Ztg., 1893*, **92**, 1691.

well adapted for the analysis of most of the American refined coppers.

The process depends upon the removal of most of the copper as cuprous sulphocyanate.

The manner in which I practice it is briefly as follows:

Twenty-five grams of material are placed in a tall, lipless beaker and treated with a mixture of 200 cc. of water, forty-five to forty-six cc. of nitric acid (sp. gr. 1.21), and twenty-five cc. of concentrated sulphuric acid (in case that much antimony or bismuth is present, as much as 100 cc. of sulphuric acid may be taken). The beaker is covered and heat applied until nitrous fumes are no longer given off and the solution then diluted with 200 cc. of water to prevent the separation of copper sulphate. A rapid current of sulphur dioxide is now conducted into the liquid, the temperature of which is maintained at about 40° C. When the nitric acid is destroyed and the red fumes have disappeared, the liquid becomes turbid, owing to the precipitation of silver, selenium, and tellurium. To insure the complete separation of the silver, a drop or two of hydrochloric acid may be added. After standing for twenty-four hours in a warm place, the solution is poured through a small filter into a graduated flask of two liters capacity. It may contain bismuth, antimony, arsenic, iron, nickel, and cobalt.

The sediment retained by the filter is composed of gold, silver, silver chloride, selenium, tellurium, possibly also lead sulphate, and traces of bismuth and antimony.

To determine the elements in the filtrate, the greater part of the copper must first be removed. To this end a measured amount of standard potassium sulphocyanate solution (one cc.= 0.05 Cu) is gradually added, whilst a current of sulphur dioxide is passed into the liquid. An excess of the sulphocyanate should carefully be avoided; it is preferable to leave some of the copper in the solution which should now emit a perceptible odor of sulphur dioxide. The delivery-tube is withdrawn and rinsed off into the flask, the contents of which are then made up to the mark. To effect a thorough mixing it is well to pour the contents into a dry beaker, and to retransfer them several times from one vessel to the other. The precipitate is allowed to set-

tle and an aliquot portion, say 1,800 cc. of the solution, filtered off. The separation and estimation of the different metals is effected according to the usual analytical methods. It is hardly necessary to state that the sulphur dioxide must be expelled before hydrogen sulphide is passed into the liquid.

In calculating the amounts of the metals contained in the entire liquid, we must allow for the volume occupied by the precipitate. According to Hampe, the specific gravity of the sulphocyanate is nearly three, and since twenty-five grams of copper would give about forty-eight grams of this salt, the volume of the latter would be sixteen cc. The actual volume of the solution, therefore, is $2{,}000 - 16 = 1{,}984$ cc. Suppose *e. g.*, we had filtered off 1,800 cc., and found in it 0.020 gram of arsenic, then

$$\frac{1984 \times 0.02}{1800}$$

would be the amount of arsenic in the sample taken.

There yet remains to describe the analysis of the insoluble portion from which the main solution was filtered. It may contain, as I have already said, gold, silver (both in the metallic state and as chloride), selenium, tellurium, lead sulphate, and traces of bismuth and antimony, occasionally also copper.

It is best to detach, as completely as possible, the dry mixture from the filter, and to destroy the latter with fuming nitric acid in a small porcelain casserole. The detached portion is then added, and treated with the nitric acid till completely oxidized. After evaporation on the water-bath of the free nitric acid, the residue is digested with dilute hydrochloric acid, which leaves the silver in the form of chloride. This is filtered off, purified, and determined in the usual way. From the filtrate, selenium and tellurium may be thrown down by means of hydroxylamine hydrochloride. In the cold this reagent seems to have little effect, but upon warming, a reddish turbidity is observed which gradually collects in the form of dark flakes. These represent all the selenium and tellurium; they are collected on a tared filter and dried at 105°–110° C. to constant weight.

I have not been able to effect a clean separation of the two elements. Approximate estimations were made by fusing the

mixture in a current of hydrogen with potassium cyanide; the aqueous solution of the fused mass was then exposed to the air, which causes most of the tellurium to separate.

Gold, lead, and the traces of antimony and bismuth are determined by the ordinary methods.

NEW BOOKS.

SELECT METHODS IN CHEMICAL ANALYSIS, CHIEFLY INORGANIC, BY WILLIAM CROOKES, F. R. S., ETC., ETC.; EDITOR OF "THE CHEMICAL NEWS." Third edition, rewritten and enlarged; illustrated with sixty-seven wood cuts. London, and New York; Longmans. 1894. Price $8.

This book is without padding and is but a bare, yet voluminous, statement of analytical fact. It is sufficiently explanatory to meet the wants of the average worker. It is minute in important details. It gives concise and clear, yet full, directions for separation and determination of all known elements, and has something to say of the hypothetical ones. And while but little is stated concerning those processes well understood by analysts, there is set forth about all which concerns the newer and verified ones. The book contains a skillful digest of the best of analytical literature down to the middle of the present year.

After the preface, come thirteen pages of index to captions. The next forty-two pages are given to potassium, sodium, lithium, cesium, rubidium, and ammonium, stating several methods for determination of each of them when found in various combinations. Chapter II relates to barium, strontium, calcium, and magnesium. The third chapter gives sixty-eight pages of the masterly digest of the literature pertaining to cerium, lanthanum, didymium, samarium, thorium, glucinum, the yttrium metals, titanium and zirconium. In all, there are 697 octavo pages of analytical methods and processes, followed by a copious index to subjects and to authors' names. There is little risk in stating that the advanced worker will here find, at least, something he did not before know regarding his own immediate field. The volume is invaluable.

The author has something to say to him who is constrained to use chemistry as the carpenter does his rule, and the least

possible of it; but he has a great deal more to say to him who desires a higher and better knowledge. He forgets how profoundly we are taught that matter is divided into common and rare elements. He keeps before him the necessity of giving to all forms of matter the same kind and quantity of study. Realizing that most rare elements are rare in quantity only, and that their distribution is indeed wide, he has given us the only English-written book to which workers in chemical and metallurgical technology can, under all circumstances, refer: workers whose necessities require that they shall be as familiar with many rare elements as they are with iron and with oxygen.

The great majority of American chemists regard Prof. Crookes as an honest and earnest and most consummate analyst. The small remainder, which does not so consider him, consists of those who do not know his work. One consults him with the comfortable feeling that his statements already are verified, that they have come out of his laboratory note-book, and that if possibly he should not give the solution of the problem in hand, he quite surely will teach enough to make the remainder apparent.

In the preface to this third edition, the author states that he desires the volume to be regarded chiefly as a collection of novel or little-known processes which have been found to be successful. He has not set himself the task of printing again that which may be found abundantly in special literature; except, that he has felt impelled to give to the world a series of electrical separations and processes. After a critical examination of the volume, the reader will emerge with a consciousness that the author kept to his assigned task and that his work was well done.

WILLIAM GLENN.

BALTIMORE CHROME WORKS,
October, 1894.

A CHEMICAL AND METALLURGICAL HANDBOOK. By J. H. CREMER, M.E., and G. A. BICKNELL, B.Sc. pp. 280. Cleveland, Ohio: J. B. Savage. Price, $2.50.

This book contains 280 pages of information chiefly in notes and tables, which is of especial importance to iron chemists and metallurgists, and which any practical chemist or metallurgist

needs in a form convenient for reference. The extended and successful experience of the authors in the chemistry and metallurgy of iron is an assurance of reliability.

In the tables of logarithms and reciprocals, factors and logarithms for the calculation of analytical results, the specific gravity of solutions, and in the table giving the molecular weights, specific gravity, melting-points, boiling-points, and solubility of the principal inorganic compounds, chemists will find much useful information. The tables for the analysis of iron ores facilitate the calculation of phosphorus, silicon, and sulphur. Moisture tables are inserted for the calculation of the percentage of iron, silicon, manganese, and other constituents in the ore in its natural condition from analysis of the dried ore. As an example of the careful effort expended in the preparation of this book, the phosphorus table gives the percentage of phosphorus in pig-iron, from the percentage of phosphorus and the percentage of iron in the ore, for a difference of 0.001 per cent. from 0.001 per cent. up to 0.100 per cent. Other data include a table of fractional parts of numbers in tenths from one to eighteen for the calculation of phosphorus and silicon in an ore burden, and a table which gives the cost per unit of iron from the price and analysis of the ore in differences of one-half per cent., or iron from forty to seventy per cent.

For the convenience of metallurgists and prospectors in the field, a brief outline of the principal geological formations is included. The principal minerals are given with their chemical composition and physical properties. Other tables contain the amounts of limestone required to produce slags of different composition, the quantity of slag produced, and numerous other data that every blast-furnace manager must have constantly at hand. Brief notes on the properties and mutual relations of carbon, silicon, sulphur, phosphorus, and manganese in blast-furnace practice, contain much useful information. The book is well printed and neatly bound. CHARLES F. MABERY.

NOTES.

Changes in Official Methods of Soil and Ash Analysis.—The following are the principal changes in methods of soil and ash analysis adopted at the last meeting of the Association of Official Agricultural Chemists:

1. A sieve with circular openings one-half mm. in diameter is to be used in preparation of the fine earth for analysis.

2. Moisture is to be determined in the air-dried, prepared sample by drying a weighed portion to constant weight in a water-oven, the water of which is kept briskly boiling.

3. The digestion is to be done in a flask provided with a return condensing tube and heated for ten hours continuously in boiling water; ten grams of soil and 100 cc. of HCl of sp. gr. 1,115 are to be used, and the solution is to be made up to 500 cc. and aliquots taken for analysis, except where the insoluble residue exceeds ninety per cent., in which case twenty grams are to be used with 100 cc. of acid. Larger quantities of soil may be used if the proportion of acid and amount of dilution be preserved.

4. The silica soluble in Na_2CO_3 solution is to be separated before the ignition of the "insoluble residue" in both ash and soil analysis.

The methods of analysis are essentially the same as those provisionally adopted for the past two years, but as they have been rewritten and revised, it is necessary to refer to the forthcoming proceedings for the details. The proceedings are now in the hands of the printer and will soon be ready for distribution.

The recommendation of the reporter, that the question of the determination of available P_2O_5 and K_2O in soils, particularly by the action of dilute organic acids, be made one of the subjects for investigation next year, was also adopted.

ALFRED M. PETER,
Reporter on Soil and Ash, A. O. A. C.

LEXINGTON, Ky., Oct. 3, 1894.

ERRATUM.—Page 650, October 1894, fifteenth line, for *Amelia* read *Amherst.*